

REMOVAL OF THORIUM BY GANODERMA LUCIDUM AND ITS IMMOBILISATION

by

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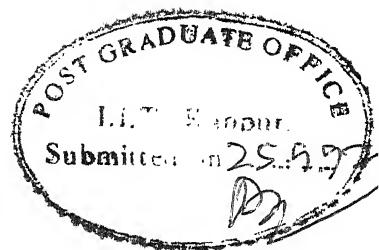
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REMOVAL OF THORIUM BY GANODERMA LUCIDUM AND ITS IMMobilISATION

*A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY*

by
SHIV KUMAR BHARGAVA

to the
Department of Nuclear Engineering and Technology
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
SEPTEMBER, 1992

Certificate

Certified that the work presented in this thesis
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Immobilisation" by Shri Shiv Kumar Bhargava has been carried
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Nomenclature

c_e	Concentration of sorbate in solution at equilibrium
c'	Predicted value of sorbate concentration in solution at desorption equilibrium
K'	Conditional stability constant
K_f	Constant related to the sorption capacity in Freundlich isotherm
L	Ligand
L_b	Bound ligand concentration
L_f	Free ligand concentration
n	Constant related to sorption intensity in Freundlich isotherm
q_e'	Predicted value of sorbate concentration retained on the sorbent per unit weight of sorbent at desorption equilibrium
q_e	Amount of sorbate adsorbed/retained per unit weight of sorbents
q_T	Amount of sorbate adsorbed
V	Volume of solution
w	Sorbent dose, mass of sorbent per unit volume of solution.

Abstract

Removal and recovery of thorium from dilute aqueous solutions employing non-viable fungal biomass Ganoderma lucidum and immobilization of spent biomass by its incorporation in cement concrete, without additives has been attempted. Kinetic studies revealed that the sorption was extremely rapid with over 90% being attained in less than 10 min. The specific thorium uptake of G. lucidum is determined to be 130 mg of Th/g of sorbent at a residual Th concentration of 700 mg/L at pH of 4.5. The presence of Cu, Zn, Ni reduced the sorption capacity of G. lucidum to a certain extent in the order of Zn > Ni > Cu. Specific Cu(II) uptake decreased with increase in residual Th concentration and vice versa. Reversibility of sorption process was investigated by employing the same sorption solution but devoid of Th for desorption, and sorption process was found to be irreversible. Eluants 1.0 N H₂SO₄ and 0.2 N Na₂CO₃ could almost completely desorb the sequestered thorium. Viability of immobilisation of spent biomass by incorporation in cement concrete, was established by carrying out short term leaching test using 0.2 N Na₂CO₃, 0.1 N HCl and simulated sea water as leachants.

Key words: Biosorption, Ganoderma lucidum, Thorium, Immobilization, Short term leaching test.

1. Introduction

At present 17% of the electricity generated in the world is, through nuclear sources. Uranium-235 is the only fissile nuclide found in nature, occurring with an isotopic abundance of 0.72% (Lamarch, 1985). The reserves of uranium (U) are limited hence the use of fast breeder reactors and/or use of thorium (Th) as fuel is strongly envisaged. Th is converted to U-233 by neutron irradiation which is a more valuable fuel for thermal reactors than plutonium. Th-U fuels have been adapted in a number of reactor systems, including the high temperature gas cooled reactor, the light water reactor, the light water breeder reactor, the heavy water reactor etc.

The increasing use of nuclear energy for electric power generation is inevitably associated with the production of radioactive wastes (rad wastes) from the various stages of nuclear fuel cycle, like mining, milling, reactor operation, spent fuel reprocessing etc. These wastes are categorized as high level wastes and non-high level wastes.

High level wastes are generally considered to be those liquid wastes resulting from the first cycle of solvent extraction system or concentrated wastes from subsequent extraction cycle, in reactor fuel reprocessing. It is immobilized in vitrified blocks and finally disposed in deep repositories. The non-high level wastes refers to liquid and solid radwastes from mining and milling, fuel fabrication facilities and reactor-operation.

The liquid low level wastes (LLW) arising from different sources have varying compositions. LLW arising from mining of uranium and thorium contain cation like Cu, Zn, Ni, As, Cr etc. and anions like HCO_3^- (in alkaline leach process), SO_4^{2-} (in acid leach process) etc. along with 10 to 100 mg/L of U and Th (IAEA Safety Series, 44, 1976). LLW arising from nuclear reactors depends on type of reactor and contain activated structural, moderator and coolant materials; corrosion products, fission products (Kr, Sr, Cs etc.) and low concentration of actinides (U, Th and trans-uranics) arising from the fuel (IAEA, Technical Report Series, 1980).

LLW are currently being treated by various physical and chemical methods such as filtration and centrifugation, ion-exchange, evaporation, chemical treatment etc. The main disadvantage of ion-exchange resins is their cost while for other chemical process, though the costs are generally lower but the decontamination factors are also lower and hence considerable effort may have to be expended on the solidification and disposal of sludges. Hence there is a need for continuing research to evolve new and effective methods for the treatment of LLW.

A recent development in environmental biotechnology is the utilisation of microbes (viable or non-viable) for removal and recovery of heavy metals. Selected fungi, bacteria, yeast and algae possess the ability to concentrate the heavy metal ions in general and radionuclides in

particular, (Tsezos and Volesky, 1981; Tobin et al., 1987; Guibal et al., 1992) and this phenomenon is termed as biosorption. It was observed that uranyl ion could be very efficiently desorbed from biomass using Na_2CO_3 (Tsezos, 1984; Tsezos et al., 1989). Thus biosorption and desorption offer a potentially efficient and economical route to removal and recovery of radionuclides from nuclear waste streams and other sources like sea-water.

The present investigation is, therefore, undertaken with the objective of evaluating the potential of a naturally occurring fungal biomass Ganoderma lucidum for removal of thorium from low level liquid waste and immobilization of spent biomass by incorporation in solid matrix. Thorium was taken as model metal because it is a potential nuclear fuel, exists in considerable quantity in uranium ore and serves as a representative element for actinides.

2. Literature Review

2.1. Scope

At present about 17% of the electricity generated is through nuclear sources in the world. Among the nuclear fuels only uranium is used commercially but owing to its limited reserve, utilization of thorium is bound to occur in future. The increasing use of nuclear energy for electric power generation, as well as the expanding application of radioisotope in various fields, are invariably associated with the production of large quantities radioactive (rad) wastes. One such type of radwaste is large quantities of low level wastes which are currently being treated using various physical and chemical methods.

The use of microorganisms to treat low-level radwastes has received much attention recently. Biosorption is a relatively new phenomenon that offers enormous scope for potential application in treatment of low-level wastes. The current information together with biosorption as emerging technology is being presented in this chapter.

2.2. World Energy Scenario

In order to discuss the power requirements and available fuel supplies on a global scale economists have chosen the unit 'Q', which is equivalent to the energy produced by burning 46,500 million tons of coal, producing approximately 300 billion (3×10^{14}) Kwh of electrical energy (Hunt, 1975). It is estimated that from the birth of Christ to the

beginning of the Industrial Revolution (1850 A.D.), the world consumption of energy was approximately 4 Q and during this time little if any, use was made of the resources of coal, oil, natural gas etc., the so-called fossil fuels. By 1850, the rate of fuel use was 1 Q per century, and a hundred year later (1950) the consumption has increased to 10 Q per century. In one year alone (1970) the consumption was approximately 0.2 Q (20 Q/century) and in 2000 it is expected to be 60 Q/century (Hunt, 1975). This means that about the year 2050 we are likely to exhaust out the conventional fuel supply (Murray, 1988). Thus the provision of additional sources of fuel to support our increasing population is one of the major problems of coming century, and solution lies in utilising alternative source of energy. In our present state of knowledge the use of nuclear-energy process appears to be most promising solution.

The total nuclear capacity in 16 of OECD countries (Organisation for Economic Co-operation & Development) is now over 247 GW, about 17% of the total electric-power capacity. The world position for nuclear power as of end of 1988 shows 429 reactors in operation representing a total 310,812 MWe (Walton, 1989).

2.3. Nuclear Fuels

Only one fissile nuclide U-235 is found in nature, where it occurs with an isotopic abundance of 0.72%. The remainder of natural uranium except for a trace of U-234 is U-238, thus only one uranium atom out of 139 is U-235.

The world reserves of uranium are not sufficient to meet the anticipated future demand for more than one century, if nuclear power is based on fission of U-235 alone (Lamarsh, 1985). From the standpoint of efficient use of limited uranium resources and to produce energy for centuries to come it is clearly preferable to employ fast-breeder reactor using U and Pu and the thermal breeder reactor, using Th (thorium) and U-233. It is conceivable that breeder reactor could buy the time needed to fully develop the alternative sources such as nuclear fusion, solar power and geothermal energy etc. (Murray, 1988). Thus in the following section the need and importance of thorium is discussed in detail.

2.3.1. Need for Thorium as a Reactor Fuel

Current interest in thorium reactors throughout the world stems largely from the fact that U^{233} produced by neutron capture in thorium is a more valuable fuel for thermal reactors than the plutonium from capture in U^{238} . Because of the high net neutron yield (n) of U^{233} in thermal reactors relative to either Pu^{239} or U^{235} , the thorium- U^{233} fuel system has higher conversion ratios and longer fuel life than is possible with U^{238} based fuel systems. Thorium reactors, therefore, are expected for long-term purposes to have lower fuel cycle costs than many uranium convertors using natural or slightly enriched uranium or uranium with recycled plutonium.

Thorium reactors have an additional advantage namely in advanced thorium converters it may be possible to breed

U^{233} sufficiently to achieve a self-sustaining recycle system whereby no supplementary input of enriched material would be required. The establishment of thorium-based power systems may make several countries with small domestic sources of fissile material self-sufficient with regard to import of nuclear fuels.

The favourable neutronic property of U^{233} not only helps in reducing fuel cycle costs but also lead to more efficient utilization of low cost uranium reserves which necessarily form the basis of all nuclear power systems that exploit only fission chain reactions. Besides low cost thorium reserves are presumably larger than that of uranium. The high conversion ratio of thorium systems could thereby lower the uranium-ore consumption. Thus, the introduction of thorium converters into nuclear power systems can delay the exhaustion of uranium ore and at least provide sufficient time required for the development of commercially competitive breeders (IAEA, 1966).

In the long run, thermal breeders using thorium are also an attractive alternatives, to the fast breeders primarily because of the smaller amount of fissile inventory required per megawatt of electrical capacity. This makes it possible to establish a self-sustaining breeder industry (i.e. one which produces all of its fissile requirements) with a considerable smaller investment, than is with fast breeders. Corresponding fuel investment costs are also lower. In addition extensive resources of thorium exist in many countries, which are adequate to support

large-scale nuclear power system for many centuries. Because of these many advantages, the advanced thorium converter thermal-breeder line of development represents an attractive approach to competitive long-term nuclear power (IAEA, 1966).

Forms of thorium which have been investigated for application in nuclear fuels are Th-U alloys, $\text{ThO}_2\text{-UO}_2$ mixtures in metal clad fuel rods, molten-salt fuels with thorium and uranium dissolved in a mixture of molten fluoride salts (IAEA, 1970).

2.3.2. Thorium Utilisation Plan by D.A.E., India

It is estimated that India has ThO_2 reserves of 450,000 tons (IAEA, 1969) mainly as monazite. The processing of this ore to produce ThO_2 and thorium metal in the forms of rods and pellets has been carried out on industrial scale.

In order to utilise its vast thorium reserves, it has planned a three stage programme. In the first stage, Pressurized Heavy-Water Reactors (PHWR) use natural uranium fuel to produce electricity, Pu-239 with 96% unused U-238. The use of Fast Breeder Reactors in the second stage with Pu-239 as fuel will generate electricity and more Pu-239 from U-238, kept as a blanket. The second stage also produces U-233 fuel from Th-232. In the third stage, U-233 will be used as fuel and Th as blanket, producing more U-233 fuel than fuel consumed in fast and thermal reactors (NPC-83A/90R).

2.4. Management of Radwastes

2.4.1. Objectives of Nuclear Waste Management

As a result of operation of nuclear reactors, radionuclides generated may be contained in the material and/or contaminate the environment. The material thus affected by radionuclides are termed as radwastes, if no further use is foreseen. The waste management has two-fold objectives (IAEA, 1980). They are: (a) Operational safety - The handling, storage, treatment, conditioning, discharge, transport and disposal of all forms of radwastes shall be carried out so that radiation exposure either to plant personnel or to others shall be as low as reasonably achievable, and (b) Environmental safety - Radwastes shall be managed so as to minimize long-term environmental effects and the efforts needed by the future generation in managing these wastes.

The following sections deal with the source of waste generation, current method of treatment along with emerging technologies etc.

2.4.2. Sources and Generation of Wastes from Nuclear Reactors

2.4.2.1. Liquid Waste

A sizeable inventory of fission products accumulates in the reactor fuel during burn-up. Since the cladding is only a fairly thin metallic sheath around the fuel, which is subjected to thermal stresses, mechanical forces, internal gas pressure, as a result small cracks develop that permit a small but finite fraction of

fission products to leak into coolant (IAEA, 1980). Thus significant radioactivity appears in the primary coolant of the reactors. Minor amounts of this liquid can leak and as a result radioactivity appears in various other streams entering the environment. Leakage from reactor system handling heavy water (i.e. reactor using D_2O as moderator or coolant) give rise to tritium (3_1H) bearing wastes.

Additional liquid waste arises during the decontamination of equipments, repair and maintenance of contaminated reactor circuits and house-keeping (Gilmore, 1977).

2.4.2.2. Solid Wastes

The handling, treatment and conditioning of liquid and gaseous wastes results in the production of considerable quantities of solid wastes. These wastes include used filters, spent ion-exchange resins, evaporator bottoms and other residues and sludges. Another source of solid waste is the accumulation of miscellaneous papers, rags, clothings etc. used during the operation and maintenance of the facilities.

2.4.2.3. Gaseous Wastes

Gaseous radioactivity appears in the off-gas streams of the reactor and ventilation systems. The main condensor off gases from Boiling-Water Reactor (BWR) and coolant clean up circuits in gas-cooled reactors and pressurized-water reactors contain mostly fission products such as Xe, Kr, I and normal gaseous activation products such as 3_1H , ^{13}N , ^{16}N , ^{17}N , ^{19}O etc. (Gilmore, 1977; IAEA, 1980).

2.4.3. Current Treatment Practices for Liquid Wastes

2.4.3.1. Filtration and Centrifugation

Filtration may be used as treatment option for all types of radioactive liquid-wastes either independently or as a pretreatment prior to ion-exchange or evaporation process. Some filters can be back-washed and the resultant sludge should be categorized as solid active-waste. However, if cartridge filters which are normally non-regenerable, are employed, provision must be made for their replacements and disposal of the filters as solid-wastes (Gilmore, 1977; IAEA, 1980).

2.4.3.2. Ion-Exchange Treatment

Ion-exchange which provides a decontamination factor (D.F.) of 10-100, is widely used in power plants for treatment of radioactive wastes. This is a suitable method for wastes containing low total suspended solids(less than 1000 ppm) without surfactants, organic materials and chelating agents. The provision of filter before the resin column is desirable.

The main disadvantage of synthetic ion-exchange resins is their cost. In some cases this can be overcome by regeneration but this then requires another stage to treat the regenerated liquids. When an ion-exchange column is exhausted, the activity of liquid effluent increases sharply. There is, therefore, a need for adequate shielding of the plant and remote handling facilities are desirable for use when the spent resins are removed from the column.

2.4.3.3. Evaporation

The process of evaporation is more suitable for liquid-wastes containing high salt concentration and low suspended solids. The feed should not contain explosives or thermally unstable substances. Since the operating cost is rather high, evaporation is more suited to wastes of small volume requiring a high decontamination factor (D.F.). D.F. of between 10^3 to 10^4 can be expected for single stage evaporation.

Since the resulting concentrates are of medium radioactivity, adequate care must be taken to house the evaporators in shielded cells with provision for reliable remote handling.

2.4.3.4. Chemical Treatment

The choice of chemicals to coagulate radioactive elements from the solutions depend upon the composition of the wastes. Coagulant aids help in producing sludge with good settling and filtration properties. Chemical treatment can be a satisfactory process in cases where the total solids content of the waste is relatively high and where a large decontamination factor (D.F.) is not required, since a D.F. of only 10 is generally obtained. However, for a specific isotope with a specific coagulant, higher D.F. may be achieved. With the chemical process itself, costs are generally low but volume reduction factors are often lower in comparison with those achieved by other processes outlined above, and considerable effort may have to be expended on the solidification and disposal of sludges

resulting from chemical treatment. For many of the chemical treatment processes extensive laboratory work is required to determine optimum dosage of the chemical.

2.4.3.5. Reverse Osmosis

The use of semi-permeable membranes to concentrate the radionuclides is increasing. Concentration factors of 10 to 20 are common. In terms of separations achieved, this process is quite similar to evaporation, i.e., a purified liquid stream and a waste concentrate are obtained.

2.5. Current Treatment Practices for Solid Wastes

The treatment of solid-wastes is by immobilization in solid matrix, compaction, incineration etc., the most popular method being the former.

2.5.1. Immobilization Technologies

It involves the addition of an immobilization agent to active liquid or solid (wet or dry) wastes in a process which results in the formation of a free-standing, monolithic homogeneous matrix with lower leaching rates than the unprocessed waste. The major immobilizing agents in use include urea-formaldehyde (U-F) resins, hydraulic (portland) cement and cement plus additive and bitumen (Oyen, 1975; IAEA, 1980). The salient features are presented in Table 2.1. Two other processes used to immobilize waste-liquids involve use of absorbents and evaporation to a salt cake. The latter process is not used commercially, but it is being used to immobilize sodium salt solution accumulated during EDRA's plutonium production operations (Petrie et al.,

Table 2.1

Comparison of Available Immobilization Technologies

Comparison factor	Portland cement with additive	Bitumen	Thermo-setting	Urea formaldehyde
Shelf life of immobilizing agent	Long	Long	Long	Short (months)
Mix fluidity	Poor	Fair	Fair	Good
Mixer cleanability	Poor	Fair	Fair	Good
<u>Chemical tolerances</u>				
Boric acid solution	Poor	Good	Good	Good
Na ₂ SO ₄ solution	Fair	Fair	Good	Reduced efficiency
NaNO ₃ solution	Good	Fair	NA ¹	Fair
Alkaline solution	Good	Good	Good	Poor (pH adjustment)
Laundry det. solution	Poor	Fair	Good	Poor
Organic liquid solution	Poor	Good	Good	Poor
Ion-exchange resins	Fair	Fair	Good	Good
Sludges	Good	Good	Good	Good
Volumetric efficiency	0.5	>2	1 to 2	0.6 to 1
Product form	Monolith	Monolith	Monolith	Monolith
Product density (Kg/m ³)	1500-2000	1100-1700	1200-1500	1000-1300
Water binding strength	Good	Water evaporated during preparation	Fair	Fair

Table 2.1 continued

Comparison factor	Portland cement with additive	Bitumen	Thermo-setting	Urea formaldehyde
Residual free water	Seldom	Seldom	Occasionally	Occasionally
Mechanical strength	Good	Fair	High	Poor
Product stability	Good	Good	High	Poor (losses water and strength in open system)
Industrial experience	Long	Long	Beginning	15 years
Combustibility	No	Yes	Slow	Yes
Freeze/thaw resistance	Fair	High	High	Poor
Leach resistance	Moderate to Fair	High	High	Poor

1 NA = Not available.

Source: Oyen, 1975; Eichholz, 1977; Gilmore, 1977; IAEA, 1980.

1976). The immobilization technologies under development are clay fixation, glass formation and pelletization.

2.5.1.1. Development of New Cement Solidification Techniques

Although cement technology is well developed, further improvements continue to be made in the areas of improved strength, lower leachabilities, higher volumetric efficiencies and improved methods of preparation.

The development of portland cement-sodium silicate system (UNI system) by United Nuclear Industries and polymer-impregnated cement (PIC) technology by Brookhaven National Laboratory, U.S.A. (Manowitz et al., 1975; IAEA, 1980; Proc. Symp. Vienna, 1976) are one of the more promising developments.

2.5.1.2. UNI System

Its most distinguishing characteristic is the blending of concentrated sodium-silicate solution with the radwaste-cement slurry. The use of Na_2SiO_3 has three major advantages: it produces quick set with no free-water, it readily solidifies boric acid solutions, which set poorly with cement alone; and it provides a significant (30%) reduction in the solidified volume, compared with cement without additive (Heacock et al., 1974).

2.5.1.3. Polymer-Impregnated Cement (PIC) Technology

Since concrete is an open cell structure as a result of the interconnected porosity formed during the curing and therefore exposes a larger surface to leaching than is evidenced by the external geometric surface

area. Techniques have been developed to impregnate this porosity with styrene monomer which is subsequently polymerized in situ. This produces a PIC which is essentially impermeable while its strength, durability and resistance to chemical attack are significantly improved (Gilmore, 1977). PIC exhibits bulk leach rate for cesium and strontium at least two order of magnitude lower than ordinary concrete blocks.

2.6. Storage and Disposal

2.6.1. Liquid-Waste

When radioactivity of wastes is too high for disposal, they must be treated to remove most of the radio-nuclides which are converted into a solid-waste. The treated liquids may then be disposed to fresh water, coastal water and deep underground strata.

2.6.2. Solid-Waste

Whenever wastes are not to be transported off-site immediately and on site disposal is not feasible, they should be placed in suitably designed facilities such as concrete trenches, tile holes vaults etc.

In case of a reactor site with favourable hydrogeologic conditions on-site disposal of certain solid-wastes by shallow burial may be feasible.

2.7. Emerging Technology - Biosorption

Microbial cells possess the ability to bind with certain cations and remove them from solution. This potential is expressed even when the cells are dead (Polikarpov, 1966) and it is probably associated with the cell-wall

(Tanaka *et al.*, 1970; Beveridge, 1978). The phenomenon of retention of cations from solution by microbial cell (viable or non-viable) has been termed as biosorption. The transfer of metal ions from aqueous to solid biosorbent phase can be due to passive, facilitated or active transport. The mechanism of uptake can be due to physical sorption, chemical complexation with microbial-cell surface group or bioaccumulation.

2.7.1. Radioactive Metal Uptake by Viable Organism

Although application of biosorption for pollution control is recently gaining wide attention the phenomenon was observed as early as 1940's. Ruchloft (1949) observed that activated sludge efficiently removed plutonium-239 from contaminated domestic wastewater. Later, many studies on metal balance in sewage treatment plants indicated that significant amount of various metals are removed in activated sludge process (Noreberg *et al.*, 1984).

Extensive screening of microorganisms for the metal uptake has been carried out by Nakajima and co-workers (1977, 1978). They reported that ability of microbes to accumulate uranium were in the following order, actinomycetes, bacteria, yeast and fungi. Although U(VI) uptake was affected by environmental conditions such as pH and the presence of carbonate (CO_3^{2-}) ions, it remained unaffected in the presence of metabolic inhibitors, thus indicating that major accumulation of uranium is by physico-chemical means at the surface.

Many of these studies are carried with living organisms. Use of these for metal removal and recovery is not generally feasible due to certain inherent disadvantages. Wastewater containing high concentration of toxic metals with fluctuating pH are not conducive for the growth and maintenance of the active microbial population. Constant energy source in the form of organic substrates has to be provided for the sustenance of the life. Generally acid or alkali regenerants have to be used for metal recovery from these biosorbents which destroy the organisms. These lead to the attention to be focussed on the use of dead microbial mass as biosorbents.

2.7.2. Metal Removal by Non-viable Organism

Certain type of biomass are found to have a capacity of accumulating and passively binding the metals even when metabolically inactive/dead. This biosorption depends not only on the chemical composition of the cell or its components such as cell-wall but also on external physico-chemical factors and the solution chemistry of metal.

A combination of mechanism such as following may be involved in biosorption; complexation, ion-exchange, coordination, adsorption, chelation, microprecipitation etc.

(Volesky, 1987).

Non-viable cells of Saccharomyces cerevisiae and Pseudomonas aeruginosa have been shown to accumulate from 10% to 15% of its dry weight of uranium (Shumate *et al.*, 1978; Strandberg *et al.*, 1981). Rhizopus arrhizus biomass, produced as a byproduct of industrial fermentation, has a

potential for use as a biosorbent of uranium and thorium (Tsezos and Volesky, 1981, 1982). It is reported that the fungal biomass has a uranium and thorium uptake capacity of over 180 mg/g. This exceeds the capacity by 2.5 times of a common anionic exchange resin (IRA-400) used by uranium processing industries. Dead cell of Zoogloea remigera have also been examined for use in metal accumulating process (Norberg and Persson, 1984). The biomass consisting of an acidic polysaccharides was used to accumulate copper, uranyl ions and other cations.

2.7.3. Use of *Ganoderma lucidum* as Biosorbent for Metal and Radioactive Nuclides

Most of the biosorption studies reported thus far are pertaining to the use of microbes either grown in the laboratory or obtained as a byproduct from industrial fermentation or biological waste treatment process. Potential of macrofungi, which grow widely in most tropical and temperate forests, for the metal uptake is being investigated in our laboratory. Among these fungi detailed studies were conducted with Ganoderma lucidum.

G. lucidum is one of the common species of wood rotting fungi, found in different parts of the world. This fungi is non-edible and as such has no commercial value at present. Being a common variety, with no reported use, the availability is not expected to be the rate limiting. G. lucidum has been reported to have excellent Cu(II) binding properties (Muraleedharan, 1988). It has significant potential to remove other metals like Zn, Ni, Cd, Cr and Hg

Bhaskar *et al.* (1991) investigated the potential of G. lucidum for uranium uptake. It was observed that kinetics of biosorption of U(VI) by G. lucidum is very rapid with 90% of the sorption taking place in less than 10 min and attainment of equilibrium value in one hour. The sorption data fitted well to Freundlich isotherm and at a residual equilibrium U(VI) concentration of 700 mg/L in solution, the metal uptake by G. lucidum was found to be 139 mg/g. Presence of co-ions Zn, Cu, Ni marginally reduced the uptake capacity.

The uranium adsorption by different sorbent/ion-exchange resins derived from the literature is presented in Table 2.2. It shows that uranium sorption capacity of G. lucidum is significantly higher than those of activated-carbon and ion-exchange resin (IRA-400). R. arrhizus exhibited better potential (180 mg/g) than G. lucidum. However, it has been reported that bioreactors employing R. arrhizus need elaborate fluidisation techniques to maintain adequate flow rate. One of the major handicaps in the field application of biosorption technique is the difficulty in maintaining an adsorption reactor with the reasonable flow rate used in continuous flow reactors. Most biomass form sticky lumps, necessitating expensive immobilisation techniques (Shumate *et al.*, 1985). R. arrhizus required fluidisation for removal of U(VI) (Tsezos and Volesky, 1981). Pulverised mass of G. lucidum, however, did not present any such problems in a column reactor and columns could be operated over a range of flow rates. The

Table 2.2

Comparison of Uranium Uptake by Various Sorbents

Species	Uranium uptake mg/g of sorbent	References
(A) Microbial sorbents		
<u>Acinetobacter RAG-1</u>	800	Zosim <u>et al.</u> (1983)
<u>Streptomyces longwoodensis</u>	440	Friis and Keith (1986)
<u>Zooglea ramiqera</u>	370	Norberg and Person (1984)
<u>Rhizopus oryzae</u>	260	Treen-Sears <u>et al.</u> (1984)
<u>Rhizopus oligiporous</u>	250	Treen-Sears <u>et al.</u> (1984)
<u>Rhizopus javanicus</u>	250	Treen-Sears <u>et al.</u> (1984)
<u>Rhizopus arrhizus</u>	180	Tsezos and Volesky (1981)
<u>Pseudomonas aeruginosa</u>	150	Stranberg <u>et al.</u> (1981)
<u>Saccharomyces cerevisiae</u>	150	Stranberg <u>et al.</u> (1981)
<u>Pinus radiata</u> D. Don	4	Freer <u>et al.</u> (1989)
<u>Ganoderma lucidum</u>	140	Bhaskar <u>et al.</u> (1991)
(B) Chemical sorbents		
Activated carbon	145	Tsezos and Volesky (1981)
Ion-exchange resin IRA-400	79	Tsezos and Volesky (1981)
Polyhydroxy anthraquinone	40	Sakaguchi <u>et al.</u> (1986)
Composite filter and sorbent	1.560	Kobuke <u>et al.</u> (1990)

results also indicates that valuable metal could be concentrated over 20 times and column reused over many number of cycles (Sharma, 1989; Mishra et al., 1991). The recycle potential of this material is very significant from a practical point of view, as earlier reports with patented sorbents suggested digestion of the sorbent after metal uptake for recovering the metal as a strategy or necessity (Brierly et al., 1986).

2.8. Summary

Low-level radwastes generated during the processes of mining and milling of thorium and operation of nuclear reactors, are currently being treated by filtration, ion-exchange, chemical precipitation etc. Microbial biomass, that are either byproducts from food and pharmaceutical industries or grow wildly, have, however, a biosorptive potential for Th, U and TRU elements and could be used as an inexpensive material for development of an alternative treatment scheme for low-level radwastes. Used biomass, concentrating the radionuclides can be disposed off as solid waste.

3. Scope of the Study

From preceding chapter it is evident that the biosorption offers a potentially efficient and economical route to the removal of actinides from low-level liquid wastes (LLW) which contain various cation, anion, fission products, actinides etc. Spent biomass produced as a result of treatment may either be desorbed to facilitate recovery of actinides and reuse of sorbent or it may be immobilized by incorporation in suitable immobilizing agent.

The present investigation is directed to evaluate the thorium biosorptive capacity of one such non-edible wood rotting macrofungus, Ganoderma lucidum which is abundantly available in tropical forest. The studies were undertaken along the following lines:

- (i) Determination of equilibrium time for Th uptake by G. lucidum.
- (ii) The adsorption equilibria to determine Th uptake capacity by G. lucidum.
- (iii) The adsorption equilibria in presence of Cu, Zn, Ni to determine their effect on Th uptake capacity by G. lucidum.
- (iv) Effect of HCO_3^- on Th uptake by G. lucidum.
- (v) Determination of equilibrium time for Th desorption using sorption solution devoid of Th and appropriate eluants.
- (vi) Equilibrium desorption studies with sorption solution devoid of Th.

- (vii) Desorption of Th by various eluants.
- (viii) Immobilization of spent biomass by incorporation in cement concrete and carrying out short term leaching test on it.

4. Experimental Methodology

4.1. Materials

4.1.1. Biosorbents

Ganoderma lucidum, a wood rotting macrofungus collected from Kerala, India, was used as the biosorbent in the present investigation. This nonedible biomass grows on decaying trees at a very fast rate. Identification of the fungus and its microbial purity was ascertained by the Royal Botanical Garden (Kew, England). The hand picked mushrooms were washed in tap-water, dried at 50°C and pulverised to a geometric mean (GM) size of 848 μm (600-1200 μm). This material was again washed in tap water to remove any adhering impurities and then oven dried at 50°C. Non-viable biosorbent thus obtained was employed in all the experiments.

4.1.2. Reagent Solution

(a) Stock Th(IV) solution: Thorium nitrate pentahydrate (LOBA Chemie, Bombay) was dissolved in double distilled water to give a stock solution of 3500 mg/L Th(IV).

(b) Stock metal [Cu(II), Zn(II), Ni(II)] solutions: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in double distilled water to yield 500 mg/L solutions.

(c) Buffer solutions: 0.2 M acetate buffer of pH 4.5, 5.0, were prepared as per electrochemical data hand book (Dobos, 1975) using acetic acid and sodium acetate.

(d) Stock Arsenazo-III: A 0.1% solution of Arsenazo-III (John Baker Co., U.S.A.) was prepared by dissolving

100 mg dry powder in 20 mL 0.1 N NaOH, then acidifying it to pH 1.5 by using concentrated H_2SO_4 and later making the total volume to 100 mL by using 0.1 N H_2SO_4 .

4.1.3. Concrete

A M20 concrete mix was used for casting the cubes of 150 mm size. The nominal mix design method, as given in IS: 456-1978, was adopted for designing the M20 concrete mix. Proportions for M20 mix as given in IS: 456-1978 are as follows:

Cement = 50 Kg

Total quantity of aggregates

(Fine aggregate + Coarse aggregates) = 250 Kg

Ratio of fine aggregate to coarse aggregate = 1 : 2

Volume of water = 30 litres

This is equivalent to 1 : 1.67 : 3.33 concrete mix with water-cement ratio as 0.6.

4.1.4. Glassware

All glasswares used were saturated with Th(IV) by immersing it in 100 mg/L Th(IV) solution for 24 hours. After that it was immersed in single distilled water followed by several washings.

4.2. Assays

4.2.1. Thorium Assay

A spectrophotometric assay based on the reaction of thorium with Arsenazo-III was used (Shumate, 1980). The stock Arsenazo-III was diluted 1 : 10 with 0.1 N H_2SO_4 . This diluted reagent was added at a ratio of 5 : 1 (v/v) to

sample solutions that had been appropriately diluted to contain 0-4 mg/L of Th. The solutions were mixed and allowed to stand approximately 10 min, then the absorbance of each was measured at 650 nm using spectrophotometer (Model 106-Systronics, Ahemadabad).

4.2.2. Copper(II) Assay

Copper(II) estimation was carried out by Cuprethol method as given in Standard Methods (1968). The accuracy of this method is in agreement with that of Atomic Absorption Spectrophotometer. The intensity of the yellow coloured complex was measured at 440 nm by spectrophotometer -106.

4.3. Experiments

4.3.1. Kinetics of Biosorption

Sorption kinetic studies were conducted at 30°C and pH values of 4.5 and 5.0. A series of reaction bottles, containing 25 mL of 100 mg/L Th(IV), solution, 250 mg sorbent (sorbent dose of 10 g/L), 0.02 M acetate buffer was introduced in the shaker (controlled environment incubator shaker, New Brunswick Scientific Co., U.S.A.) and was agitated at 250 r.p.m. Incorporation of appropriate buffer was necessitated in the reaction mixture as the change in pH was observed.

At the predetermined intervals (5, 10, 20, 40, 60, 90, 120 and 180 min) the bottles were withdrawn from the shaker. The supernatant solution was analysed for Th after separating the sorbents by filtration.

4.3.2. Equilibrium Adsorption Experiments

25 mL of reaction mixture containing 100, 300, 500, 700, 1000, 1200, 1500, 1800, 2000, 2500, 3000, 3500 mg/L Th(IV) solution 0.02 M acetate buffer (pH 4.5), 250 mg sorbent (sorbent dose 10 g/L) were agitated in the shaker at 250 r.p.m. for the equilibrium time determined earlier. The supernatant was then analysed for Th after separating the biosorbent.

4.3.3. Equilibrium Adsorption Studies in Presence of Co-ions

The Th uptake capacity of G. lucidum was studied in the presence of metals like Cu, Zn, Ni. A series of reaction bottles containing 25 mL of reaction mixture containing 100 to 2500 mg/L Th(IV) solution, 0.02 M acetate buffer, 250 mg sorbent, 50 mg/L of Cu(II) were agitated in the shaker at 250 r.p.m. At the end of equilibrium time the supernatant was analysed for Th using Arsenazo-III assay method. Cu(II) was analysed by Cuprethol method.

Similarly other sets of experiments were conducted in the presence of 50 mg/L Zn and 50 mg/L Ni (one co-ion at a time). But the filtered supernatant was analysed only for Th.

4.3.4. Effect of HCO_3^- on Th Uptake by G. lucidum

25 mL of the reaction mixture containing 25 mg/L (0.11 mM) of Th(IV) solution and 1 mM, 2 mM, 3 mM, 4 mM, 5 mM, 7 mM and 10 mM of HCO_3^- , all at pH 8 (pH adjusted to 8 by 0.1 N HNO_3), 25 mg of sorbent were

agitated in shaker at 250 r.p.m. for 3 hours. Then the supernatant was analysed for thorium after separating the sorbent.

4.3.5. Kinetics of Desorption

Experiments consist of two stages, i.e., loading of sorbent with Th(IV) and desorption of loaded sorbent by appropriate eluant.

The sorbent (10 g/L) was loaded with Th(IV) by contacting with aqueous phase containing 100 mg/L of Th(IV) at pH 4.5 (0.02 M acetate buffer) for equilibrium time at 250 r.p.m. on the shaker. The supernatant was analysed for Th. The Th(IV) loaded sorbent was subsequently separated by filtration and then was oven dried at 50°C. The desorption kinetics was then carried out by resuspending the loaded sorbent in a series of reaction bottles containing 25 mL sorption solution devoid of Th(IV) (pH 4.5 buffered) or appropriate eluant viz. 0.2 N Na_2CO_3 . Subsequently the bottles were agitated in the shaker at 250 r.p.m. The bottles were withdrawn at the predetermined time intervals and supernatant was analysed for Th(IV). Equilibrium time for desorption was then determined and was used for subsequent experiments.

4.3.6. Equilibrium Desorption Studies

500 mg of sorbent were loaded with Th(IV) by contacting at different initial concentration (100, -1200 mg/L) of Th(IV) and at pH 4.5 (0.02 M acetate buffer). The Th(IV) loaded sorbent was filtered and dried in oven.

Desorption experiment was conducted by suspending the 250 mg of loaded sorbent in 25 mL of sorption solution at pH 4.5 devoid of Th and agitating in shaker at 250 r.p.m. for equilibrium time then supernatant was analysed for Th(IV).

4.3.7. Desorption of Th by Various Eluants

250 mg of loaded sorbent as described in Section 4.3.5 were contacted with 25 mL of 0.05, 0.1, 0.2, 0.5, 1.0 N H_2SO_4 and 0.2 N Na_2CO_3 solutions by agitating in the shaker at 250 r.p.m. After the equilibrium desorption time of 90 min, the supernatant was analysed for Th.

4.3.8. Loading of *Ganoderma lucidum* with Thorium

Loading of G. lucidum was done in a reactor containing four litre of Th solution of 2500 mg/L. Amount of G. lucidum used was 37 g. 0.02 M acetate buffer was introduced in the reactor to maintain pH of 4.5.

This mixture was agitated with the help of a Remi stirrer (at 60 r.p.m.) for 90 min. The supernatant solution was analysed for Th.

4.3.9. Casting of Cement-Concrete Blocks

Total five numbers of concrete blocks with thorium loaded sorbent placed in the central region were cast at Structural Engineering Laboratory by the following procedure:

Required amount of G. lucidum was packed in poly-ethene bag with number of holes to allow leaching of thorium freely. This was done to ensure that polyethene is not hindering the leaching of thorium. For casting, mould was

filled upto half level and vibrated thoroughly, after that polyethene bag was put at the central region. The remaining part of the mould was filled with concrete and vibrated at the corners, so that vibrations do not damage polyethene bag.

In casting the blocks proportion of the G. lucidum to cement employed was 1 percent.

4.3.10. Curing

All the cubes were cured in tap water for 7 days. During curing period samples were taken from the tank and subjected to Th(IV) determination.

4.3.11. Determination of Leachability of Thorium from Concrete Blocks in Various Aqueous Media

After 7 days of curing the cubes were put in tanks containing the different aqueous solutions. The aqueous solutions used are as follows:

- (1) Simulated sea-water
- (2) 0.1 N HCl
- (3) 0.2 N Na_2CO_3

Simulated sea-water was prepared as per the composition of Barrow (1988) and the same is presented in Table 4.1.

Na_2CO_3 and HCl solutions were used to check leachability in adverse environmental condition. Samples were taken at a time interval of one day and analysed for Th(IV).

Table 4.1

Composition of Simulated Sea-Water

Constituents	Concentration, g/L
NaCl	29.31
MgCl ₂	3.99
MgSO ₄	1.83
CaSO ₄	1.34
K ₂ SO ₄	0.85

5. Results and Discussion

The various stages of nuclear fuel cycle produce low level liquid waste (LLW) which contain actinides (Th, U, trans uranic elements), fission products, coolant activation products, cationic and anionic species etc. Thorium is considered as a model metal for actinides. If the biomass G. lucidum has the potential to remove Th, then it can be presumed that actinides can be removed. The present work is, thus, directed to evaluate the potential of naturally occurring fungal biomass G. lucidum for removal, recovery of thorium and the viability of immobilization of spent G. lucidum by incorporating it in cement concrete, without additives.

Kinetics and equilibrium sorption studies along with the studies to determine the effect of competing metal ions and HCO_3^- as anionic ligand were carried out. Different eluants were employed to recover the sorbed thorium and short term leaching tests were done on concrete blocks incorporated with spent G. lucidum. In the following sections the results on these aspects are presented.

5.1. Kinetics of Sorption

Figure 5.1 presents the residual Th concentration profile with time for pH 4.5 and 5.0 at 30°C. The Th removal was rapid with nearly 60% and 90% or more of the total uptake occurring in 5 and 30 min respectively, with attainment of equilibrium in one hour. The specific Th uptake rate for

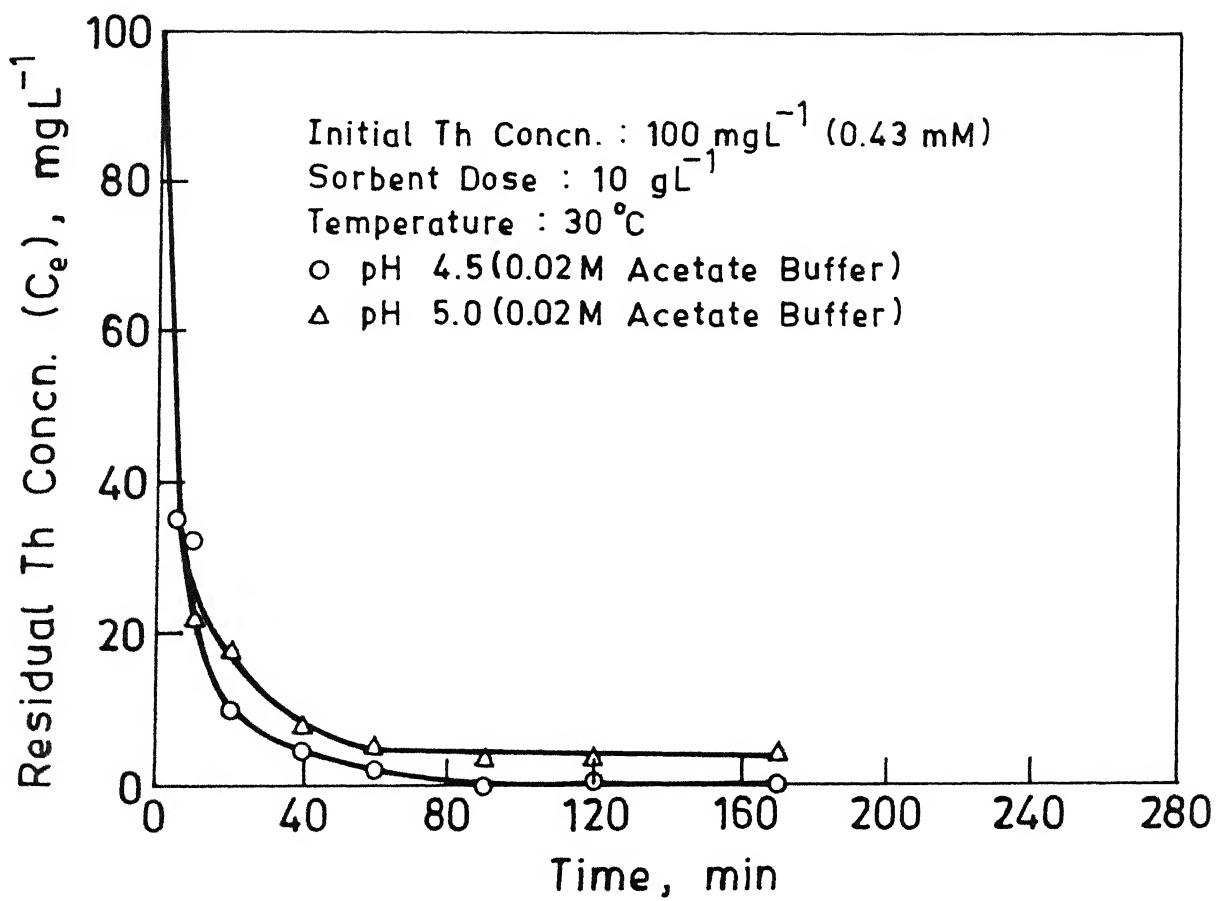


Fig. 5.1. Kinetics of Th Sorption.

initial 5 min is determined as 1.5 mg/g min for G. lucidum. Bhaskar et al. (1992) using G. lucidum reported U(VI) specific uptake rate as 1.45 mg/g min.

Table 5.1 represents Th and U uptake values for different biosorbents. It is evident that in pH range 4 to 5 the maximum uptake was exhibited by all sorbents. The highest Th sorption efficiency of 99% was obtained for G. lucidum, thus showing that it can completely scavange radionuclides at an initial concentration of 100 mg/L, which is of significant practical importance because low LLW may often contain radionuclides in this range (Ashley and Roach, 1990; Gilmore, 1977).

Thorium solubility decreases dramatically with pH (Tsezos and Volesky, 1981). At pH 2 Th(IV) solubility is high with only Th^{4+} as soluble species. Beyond this pH, the species like $\text{Th}(\text{OH})_3^+$, $\text{Th}(\text{OH})_2^{2+}$, $\text{Th}(\text{OH})_3^+$, $\text{Th}_6(\text{OH})_{15}^{9+}$ etc. are formed. However, $\text{Th}(\text{OH})_2^{2+}$ is the dominant species at pH 4.0 (Tsezos and Volesky, 1981). These hydrolysis products have a tendency to get strongly adsorbed by sorbents (Abramson et al., 1964). The kinetics of Th biosorption (Figure 5.1) by G. lucidum is also rapid indicating Th adsorption occurs without mass transfer limitations. The rapid kinetics warrants the deployment of high rate contact processes for field conditions.

In the range of pH 4 to 5 the reduction of Th(IV) solubility is small with $\text{Th}(\text{OH})_2^{2+}$ continuing to be dominant species. Therefore, the relatively small change in the

Table 5.1

Equilibrium Metal Uptake (%) by Various Microbial Sorbents

S.No.	Microbial sorbent	Metal concentration, mg/L	Metal uptake (%) at different pH				Reference
			2	4	4.5	5	
1.	<u><i>Mucor miehei</i></u>	U	100	14	65	—	90 61.5 Guibal et al., 1992
2.	<u><i>R. arrhizus</i></u>	U	42	24	48	—	— — Tsezos and Volesky, 1981
3.	<u><i>R. arrhizus</i></u>	Th	18	—	33	—	— — Tsezos and Volesky, 1981
4.	<u><i>G. lucidum</i></u>	U	100	70	94	95	— Bhaskar, 1991
5.	<u><i>G. lucidum</i></u>	Th	100	—	—	99	95 — Present work

nearly equal Th biosorptive uptake exhibited at pH 4.5 and 5.0 by G. lucidum. Similar observations were also made by Guibal et al. (1992) and Bhaskar et al. (1992) for the sorption of U(VI) by different biosorbents at pH 4.5 and 5.0. However, beyond pH 5 the solubility of Th(IV) decreases sharply (Tsezos and Volesky, 1981) resulting in the formation of precipitation of Th. This would decrease the soluble concentration of thorium causing a retardation in the sorption process. Hence the experiments were conducted in the pH range of 4 to 5.

5.2. Equilibrium Sorption Studies

Equilibrium sorption studies were conducted at 30°C and pH 4.5. Choice of pH was vital because Th dissolution chemistry involves hydrolysis which is a strong function of pH. At pH 2 thorium is highly soluble which decreases with the increase of pH and above pH 5 the solubility is very low. The biosorptive uptake of Th was meager at pH 2 (Th^{4+}) in the most examined cases using Pseudomonas fluorescens, Streptomyces niveus, IRA-400 etc. (Tsezos and Volesky, 1981). Bhaskar et al. (1992) reported that uptake U(VI) using G. lucidum at pH 2 is also meager. The plausible reason for this is that Th^{4+} has a high charge density, and since H_2O may act as Lewis base, it gets covalently bonded to H_2O , forming hydrated ion $\text{Th}(\text{H}_2\text{O})_n^{4+}$ (Katz et al., 1986). This, therefore, shows the tendency to remain in aqueous phase rather than getting sorbed onto sorbent. The later experiments on desorption of Th from G. lucidum appear to provide evidence for this. The predominant species in the pH range

of 4 to 5 is Th(OH)_2^{2+} and the kinetic experiment (Figure 5.1) has demonstrated a favourable sorption. Guibal *et al.* (1992), Tsezos and Volesky (1981) working with U and Th using various biosorbent and Bhaskar *et al.* (1992) working with U using *G. lucidum* also found the most favourable biosorption in the pH range of 4 to 5 (Table 5.1). Hence, sorption equilibrium was conducted at pH 4.5.

The sorption curves reflect the metal-biosorbent interaction and can provide the valuable information about the physico-chemical nature of sorption. Transfer of metal to sorbent proceeds till the soluble metal concentration is in dynamic equilibrium with that on the solid phase. Plot of equilibrium metal-loading by the sorbent (q_e , mg/g) against equilibrium metal-loading by the sorbent (c_e , mg/L) can be used for a good quantitative comparison of sorbents for metal uptake. The plot is presented in Figure 5.2.

The sorption curve (Figure 5.2) showed a high Th(IV) uptake featuring a steeply rising segment at relatively low equilibrium concentration, indicating a favourable uptake of Th by *G. lucidum*. It was attempted to fit the sorption data to two most widely accepted isotherm models, namely, Langmuir and Freundlich. Of these Freundlich isotherm gave a better fit. Similar observation was also made by Tsezos and Volesky (1981).

The linearised form of Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad (5.1)$$

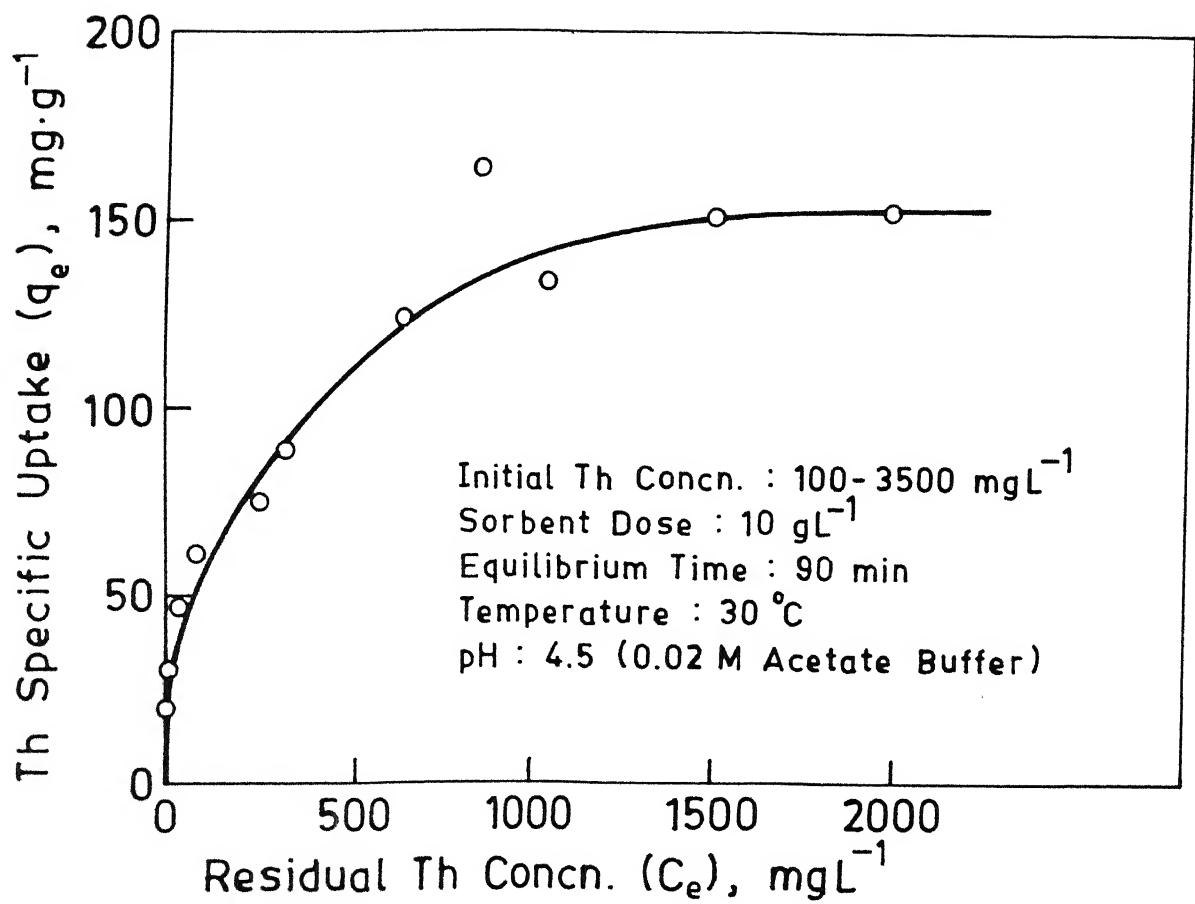


Fig. 5.2. Equilibrium Uptake of Th by G. lucidum.

where q_e = amount of sorbate sorbed per unit weight of sorbent;

c_e = equilibrium concentration of sorbate in solution.

K_f and n are constants relating to sorption capacity and intensity. The linearised plot of Freundlich equation is presented in Figure 5.3 and the empirical equation is as follows:

$$q_e = 18.81 c_e^{0.293} \quad (5.2)$$

Thorium sorption capacities of G. lucidum for a residual concentration of 30 and 700 mg/L are 50 and 130 mg/g respectively as per the above equation. The information regarding the sorption capacities of various biosorbents along with G. lucidum is presented in Table 5.2. The inspection of results shows that only Rhizopus arrhizus and P. chrysogenum exhibited the Th uptake more than G. lucidum for a residual concentration of 30 mg/L. Ionex IRA-400 exhibited only one tenth of the Th uptake capacity of G. lucidum under similar conditions. It may be mentioned that Ionex IRA-400 is commercially employed for U(VI) recovery by most uranium production companies.

5.3. Equilibrium Sorption Studies in Presence of Co-ions

LLW contain a spectrum of ions which may interact strongly with the sorbent, hence there is a need to study the effect of co-ions on the sorption of Th. The effect of metal co-ions like Zn, Cu, Ni on Th uptake was determined by carrying out the equilibrium studies at pH 4.5 in presence

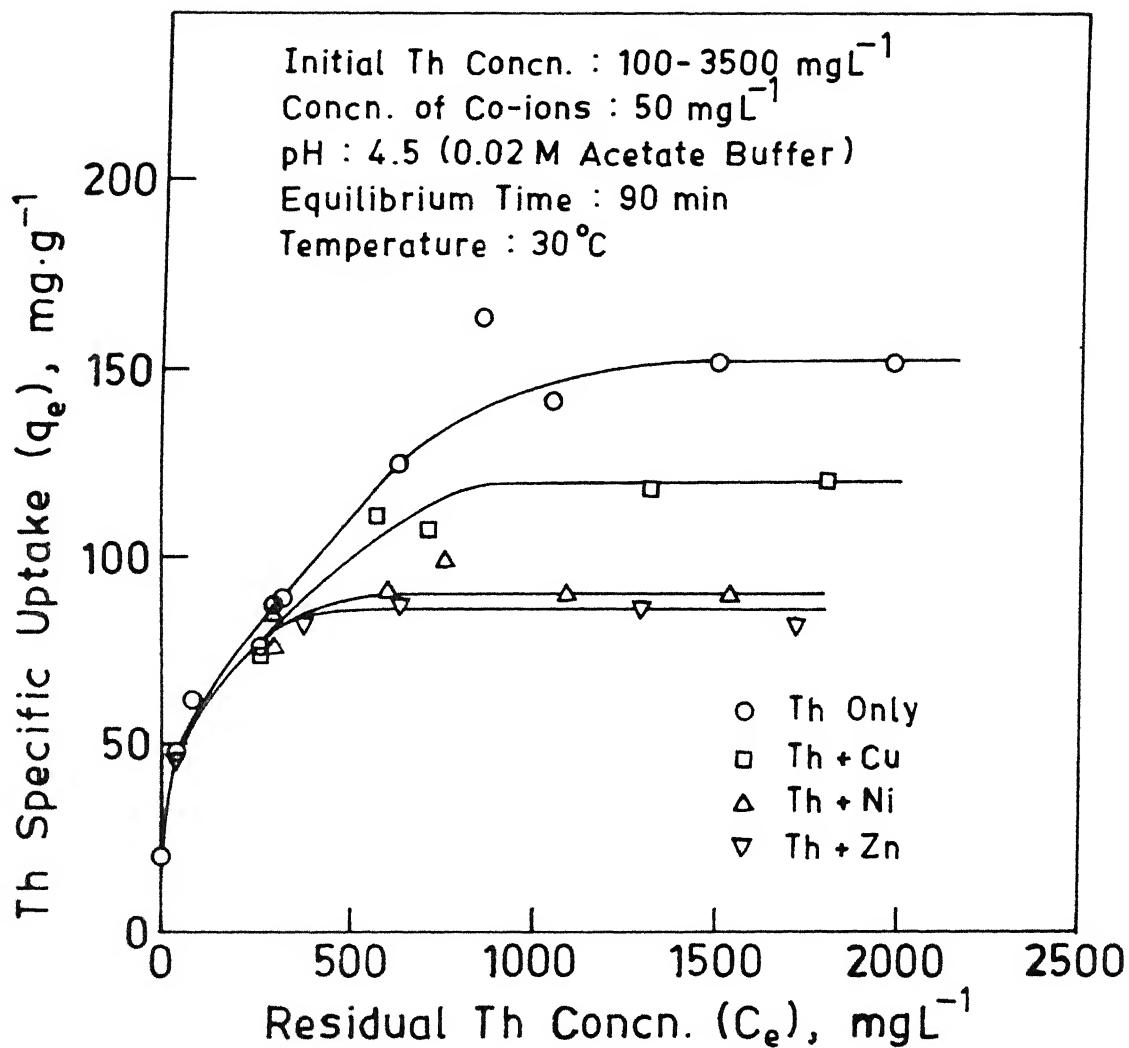


Fig. 5.3. Equilibrium Uptake of Th by G. lucidum in Presence of Co-ions.

Table 5.2

Thorium Sorption Capacity by Various Sorbents

Species	Residual conc. mg/L	Specific Th uptake mg/g	References
A) Microbial sorbent			
<u>A. terreus</u>	700	8	Tsezos and Volesky (1981, 1982)
<u>A. niger</u>	700	22	-do-
<u>P. fluorescens</u>	700	15	-do-
<u>S. niveus</u>	700	34	-do-
Municipal activated sludge	700	47	-do-
<u>P. chrysogenum</u>	30	142	
<u>R. arrhizus</u>	30	185	-do-
B) Ion-exchange resin			
Ionex IRA-400	700	14	-do-
Activated carbon F-400	30	61	-do-
C) <u>G. lucidum</u>			
	30	50	Present work
	700	130	

of 50 mg/L of each of Cu(II), Zn(II), Ni(II) at 30°C. The plots of Th uptake against residual concentration of Th are given in Figure 5.3. The experimental data were fitted to Freundlich isotherm (Figure 5.4) and corresponding equations are presented in Table 5.3.

These studies indicated that the presence of co-ions reduced the Th specific uptake of G. lucidum (Table 5.3). The decrease in Th specific uptake is insignificant at lower residual concentration being nearly 15% at $c_e = 30$ mg/L but at higher residual concentration Th specific uptake is significantly affected. The decrease in maximum Th specific uptake ($q_{e\max}$) by Cu(II), Ni(II), Zn(II) are 21%, 40% and 42% respectively. Despite of it, G. lucidum has uptake of 100 mg/g which is significant enough to justify its use as an effective sorbent for Th removal from LLW.

Tsezos and Volesky (1982) have also reported the interference of Fe^{2+} and Zn^{2+} co-ions with U and Th biosorption using R. arrhizus. Fe^{2+} and Zn^{2+} at a concentration of 100 mg/L and 50 mg/L respectively decreased the U specific uptake of R. arrhizus by 62% and 33% respectively while they caused a decrease in Th specific uptake to an extent of 14%. The co-ions Cu, Zn and Ni exhibited an antagonistic effect for Th biosorption by G. lucidum, U by R. arrhizus (Tsezos and Volesky, 1982). However, the interference for Th uptake by R. arrhizus was minimum (14%).

During equilibrium sorption studies for Th in the presence of Cu(II) as co-ion, the specific uptake for Cu(II)

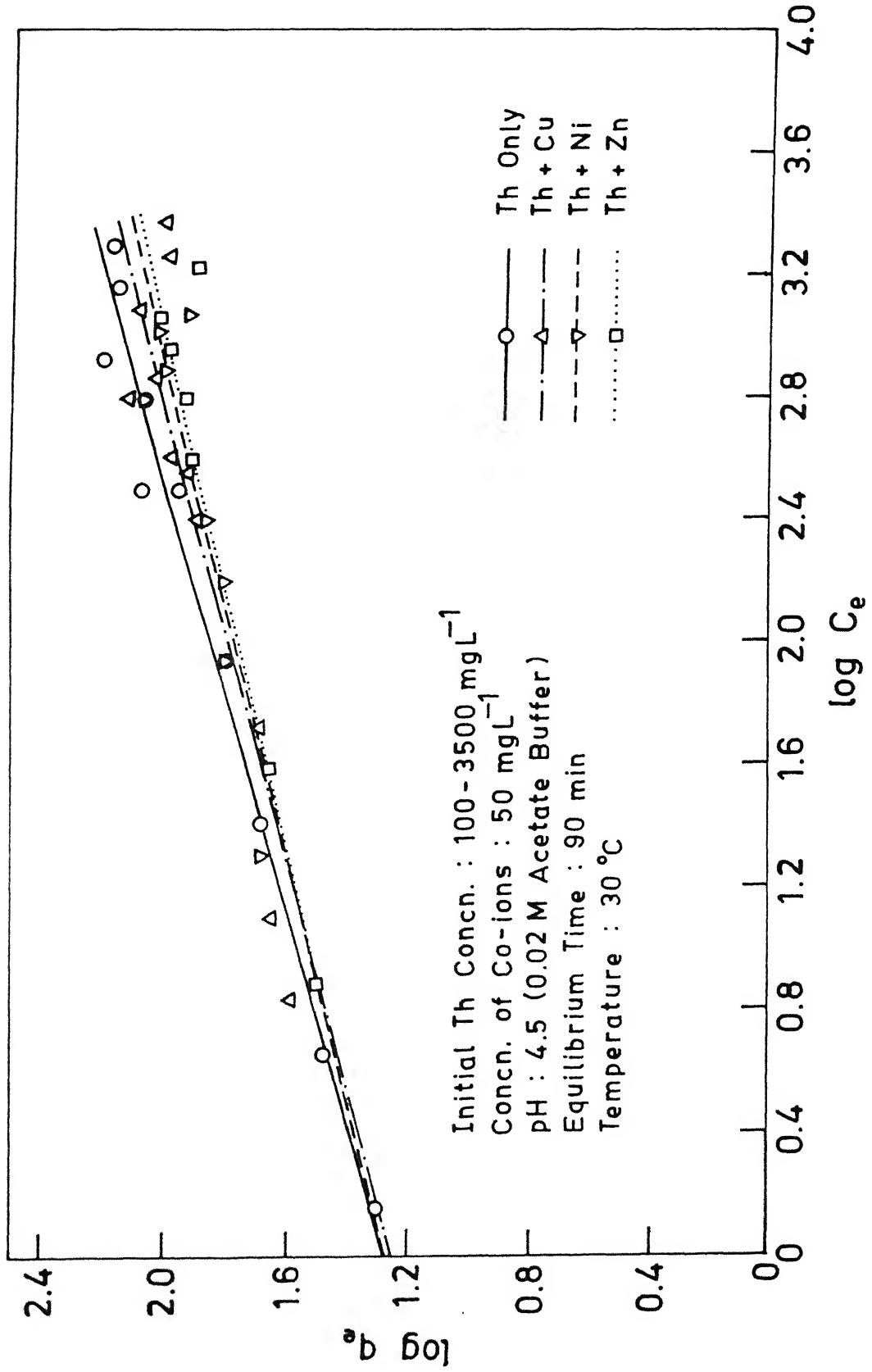


Fig. 5.4. Linearised Freundlich isotherm for Uptake of Th by G. lucidum in Presence of Co-ions.

Table 5.3

Specific Th Uptake and Sorption Isotherms for Th in Presence of Co-ions

Sorbate	Initial conc. of co-ions mg/L	temp. °C	Freundlich isotherm equation	Specific metal uptake corresponding to a residual Th concentration, mg/L	Percent decrease in specific metal uptake corresponding to a residual Th concentration, mg/L		
					30	700	1200
Th	0	4.5	30 $q_e = 18.81 c_e^{0.29}$	50	126	151	-
Cu-Th	50	4.5	30 $q_e = 17.38 c_e^{0.28}$	48	105	120	11
Ni-Th	50	4.5	30 $q_e = 18.62 c_e^{0.26}$	44	96	90	13
Zn-Th	50	4.5	30 $q_e = 18.62 c_e^{0.25}$	43	92	86	15
					27	24	40
							46

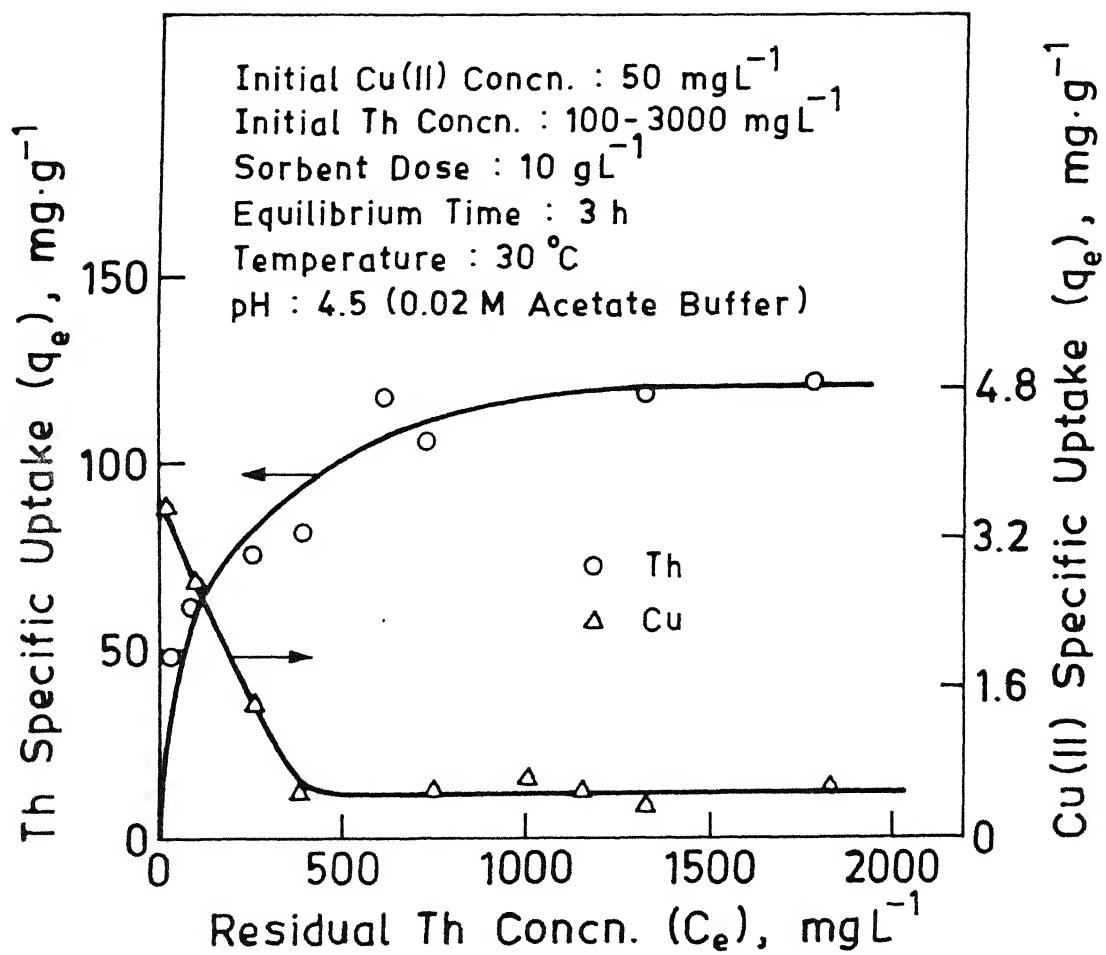


Fig. 5.5. Equilibrium Distribution of Cu(II) and Th Between Aqueous Phase and G. lucidum.

Cu(II) exhibited a specific uptake of 3.52 mg/g at a Th residual concentration of 25 mg/L, which linearly decreased with the increase in residual Th concentration upto 400 mg/L. At this stage Cu(II) uptake reached a minimum value of 0.44 mg/g. Beyond this point the Cu(II) remained constant despite of increase in Th concentration.

The biosorption involves the bulk transport of solute from solution phase to biosorbents and its subsequent diffusion (Tsezos and Deutsmann, 1992). In a system where Cu(II) concentration is kept constant, corresponding to a low initial Th concentration the proportion of Cu(II) ions in the bulk is high which leads to high specific uptake.

However, with the increase in Th concentration the proportion of Cu(II) ions in bulk transport of solute decreases leading to the observed decrease of Cu(II) specific uptake. At saturation, q_e for Cu(II) is 0.44 mg/L (6.8×10^{-3} mM/g) while the corresponding decrease in q_e for Th is 30 mg/g (0.129 mM/g) which implies that 1 mM/g of Cu(II) sorbed will cause a decrease in Th uptake by 19 mM/g. Competition for sites alone cannot explain such a disproportionate decrease in Th uptake. Beveridge (1980) suggested that chemically retained metal on the cell wall constituent of B. sutilis, may act as nucleation site for further deposition of metal on the cell-wall. Similarly Th retained or complexed to cell wall constituent of G. lucidum may be acting as nucleation sites for further deposition of Th. However, a slight decrease in the concentration of complexed Th in the presence

5.4. Effect of HCO_3^- Anion on Th Uptake by G. lucidum

The liquid waste from thorium and uranium milling operation utilizing alkaline leaching process, have approximately a pH of 8 and contains significant concentration of HCO_3^- (10 mM) along with actinides, i.e., Th, U (60 mg/L), Ra and other constituents (IAEA Safety Series, 1976). Furthermore, a number of actinides and other heavy metals can be potentially extracted from sea water ($\text{pH} \sim 8$) if an efficient and cheap sequestering agent is employed (Tsezos and Volesky, 1981). Of actinides it appears only uranium can be beneficially extracted from sea water since it is prevalent in sea water in hexavalent state and thus can form complex with CO_3^{2-} and HCO_3^- present in sea water to form $\text{UO}_2(\text{CO}_3)_3^{4-}$ with $\log K$ value of 22.8 (Ringbom, 1963), thus making sea water a potential source of uranium. Th being present in tetravalent state cannot form complex with HCO_3^- under the conditions existing in sea water hence it precipitates as $\text{Th}(\text{OH})_4^-$ (s) and thus sea water is not potential source of thorium. The same is true of other actinides (Katz *et al.*, 1986).

It has been experimentally demonstrated that G. lucidum shows a sorption efficiency of 99% at low concentration of actinides [Th, Section 5.1; U (Bhaskar *et al.*, 1992)] in absence of HCO_3^- at pH 4.5. In order to evaluate the effectiveness of G. lucidum in treating alkaline mill waters as well as extraction of precious metal from sea water sorption experiments were conducted at pH 8 in the presence of varying concentration of HCO_3^- (1 to 10 mM). The results of such

Table 5.4

The Sorption Efficiency of G. lucidum
in Presence of HCO_3^- at pH 8

Concentration of HCO_3^- in mM	0	1	2	4	10
Sorption efficiency %	98.8	97	96	93	85

of 25 mg/L (0.11 mM). The Figure 5.6 depicts the ratio of Th uptake in presence and absence of HCO_3^- . A linear decrease with the increase in HCO_3^- concentration is evident. This is because all the actinides (M) form complexes with CO_3^{2-} and HCO_3^- , namely, $\text{MO}_2(\text{CO}_3)_3^{4-}$. Th and U form the final complexes $\text{ThO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ respectively in alkaline solutions (Katz *et al.*, 1986).

The uptake ratio as per Figure 5.6 is 0.96 for HCO_3^- concentration of 2 mM while it decreases marginally to 0.85 when HCO_3^- concentration was increased to 10 mM. It may be noted that the sea water contain an average of 2 mM HCO_3^- . The reduction is, however, not very significant for G. lucidum compared to the result of Benjamin *et al.* (1985) who reported the incapability of Chlorella vulgaris, an algal biomass, to remove U(VI) from bicarbonate containing wastewaters unless the pH of wastewater is decreased to 5.

Tobin *et al.* (1986) reported similar effect from anionic ligand on sorption of U(VI) by R. arrhizus.

In fact several investigators have used HCO_3^- and CO_3^{2-} to elute actinides, U(VI) bound to biosorbent (Galun *et al.*, 1983; Nakajima, 1982; Tsezos, 1984; Bhaskar *et al.*, 1992).

The presence of anionic ligands in sorption medium can alter the metal sorption interaction in many ways:

(1) The metal ligand complexes formed may be non-adsorbing or only weakly adsorbing, leading to the decrease in metal uptake by the sorbent. The sorbent and ligand thus will be competing with each other for the metal. (2) The metal-ligand complexes - - - - -

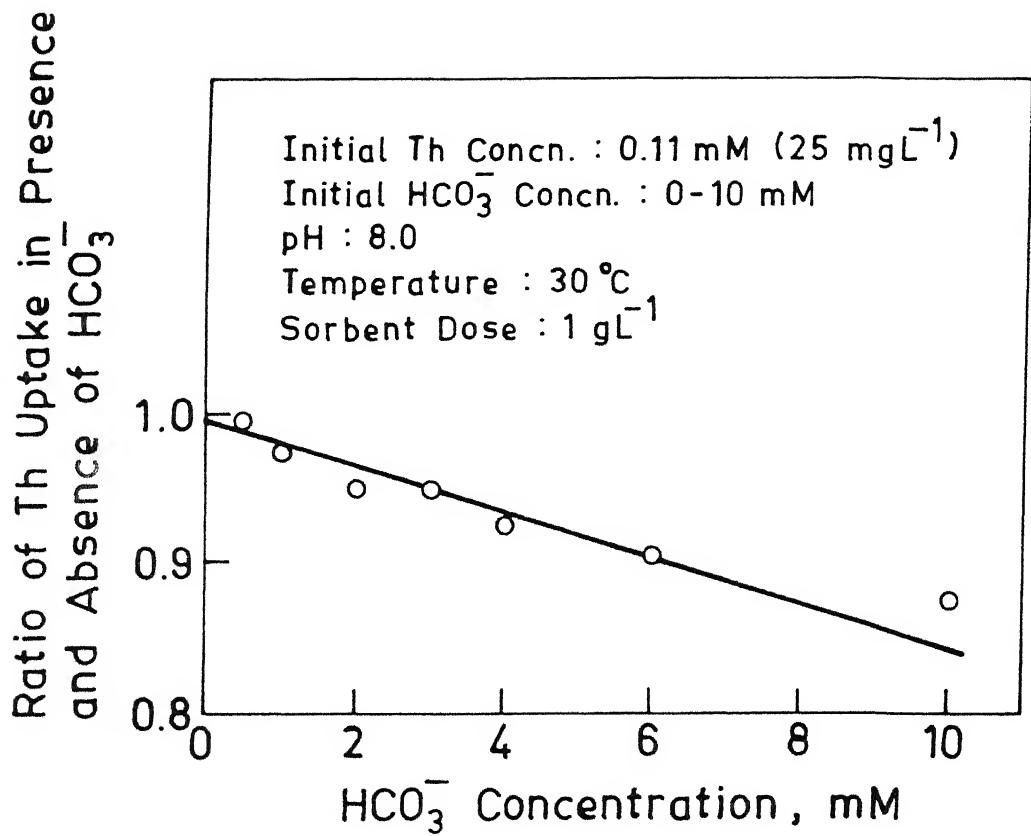


Fig. 5.6. Effect of Bicarbonate Concn. on Sorption of Th by G. lucidum.

metal, resulting in enhancement in metal uptake (Rao et al., 1992). Results in Table 5.4 shows that there is decrease in metal uptake in presence of ligands. This is to be expected as actinides complexes with HCO_3^- and these are non-adsorbing (Tobin et al., 1986).

This reason for decrease in Th uptake by G. lucidum in presence of HCO_3^- may be explained by evaluating the conditional stability constant (K) of Th-G. lucidum in the absence of HCO_3^- and then comparing it with stability constant of $\text{ThO}_2(\text{CO}_3)_3^{4-}$. The log K value for this is more than 20 (Katz et al., 1986). This value for G. lucidum-Th system is evaluated as 3.02 (Appendix A-1). It is evident from these values that HCO_3^- forms a stronger complex resulting in reduction of Th uptake by G. lucidum.

5.5. Desorption of Th from G. lucidum

The desorption of sorbate from sorbent can provide valuable information about the nature of physico-chemical interaction involved in the sorption process. McKay et al. (1987) and Mittal and Venkobachar (1992) conducted such studies for determining the mechanism of sorption between dyes and low cost adsorbents. Experiments were conducted on desorption of Th from G. lucidum to delineate the nature of interaction between them. The desorption was conducted employing two media: (i) the sorption solution devoid of Th, and (ii) alkali solution.

5.5.1. Desorption of Th Using Sorption Solution Devoid of Th

Sorption solution devoid of Th was employed to desorb the adsorbed Th from biosorbent having initial Th loading of 7.6 mg/g. The kinetic data are presented in Figure 5.7. It is evident that desorption kinetics, like that of sorption kinetics, is also rapid, with the establishment of equilibrium plateau in about 80 min. However, the desorption efficiency is very low (1.3%) even at the end of 180 min. The sorption isotherm along with a mass balance equation for sorbate can be used to predict the concentration of Th desorbed in aqueous phase. This is because Th desorption experiment involves replacing equilibrium sorption media with sorption solution devoid of Th and waiting for the attainment of new equilibrium. When this is established, the amount of Th desorbed into the aqueous phase is indicative of the degree of reversibility of the reaction. The following is the procedure adopted.

Upon initial equilibration with aqueous solution of Th, the total amount of Th adsorbed (q_T) is

$$q_T = q_e w \quad (5.2)$$

where w is the mass of biosorbent added.

If the sorption equilibrium solution is replaced by identical solution but devoid of Th, the mass balance after attainment of desorption equilibrium, then, will be

$$q_T = q'_e w + c'_e V \quad (5.3)$$

where q'_e and c'_e are the values at new equilibrium, V is the volume of desorbing solution.

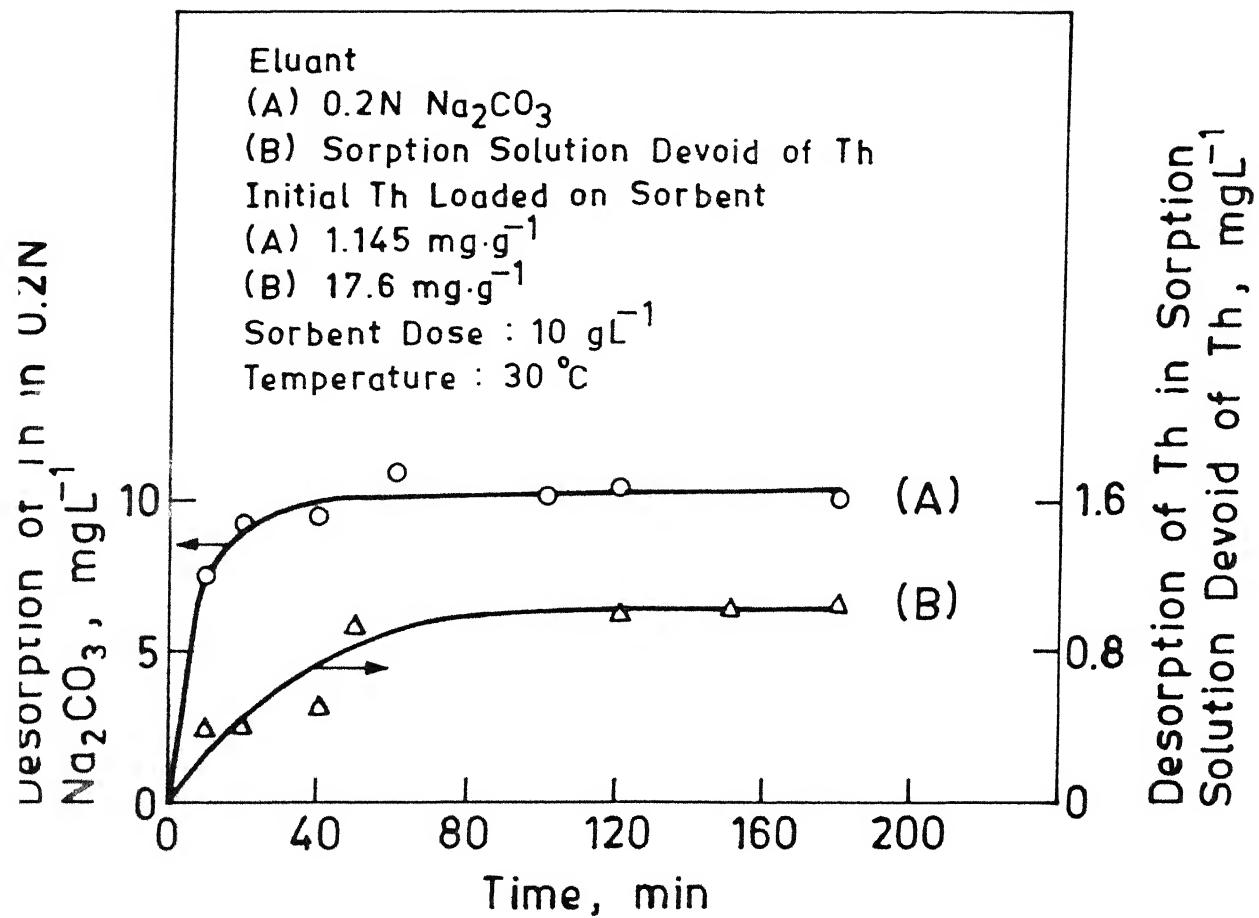


Fig. 5.7. Kinetics of Desorption of Th from G. lucidum in 0.2N Na_2CO_3 and Sorption Solution Devoid of Th.

The general form Freundlich equation is,

$$q_e' = K_f c_e'^{1/n}$$

$$q_T = c_e'^n + K_f c_e'^{1/n} W \quad (5.4)$$

$$\text{or} \quad q_T - c_e'^n - K_f c_e'^{1/n} W = 0 \quad (5.5)$$

Prediction of c_e' for a completely reversible process can be made using equation 5.5.

The plots of observed Th desorption into aqueous phase(c_e') and predicted c_e' as per equation 5.5 for different q_e values are presented in Figure 5.8. It can be observed that much less Th was released into the aqueous phase than predicted by the above model. This suggests that the Th sorption by G. lucidum involves strong chemical interaction between them. The meagre amount of Th that is, however, desorbed is indicative of physical adsorption of Th onto G. lucidum as an operative mechanism to a limited extent.

5.5.2. Desorption of Thorium from Biosorbent Using Eluants

Liquid waste from thorium and uranium mills contain approximately 60 mg/L Th and U (IAEA, 1976). The potential of waste fungal biomass G. lucidum in effectively binding Th when present in this concentration range, at natural pH and in presence of co-ions has already been described in earlier sections. Recovery of biosorbed actinides (Th, U and other trans uranic elements) from G. lucidum is a logical step in conservation of these precious metals besides eliminating hazards associated with disposal

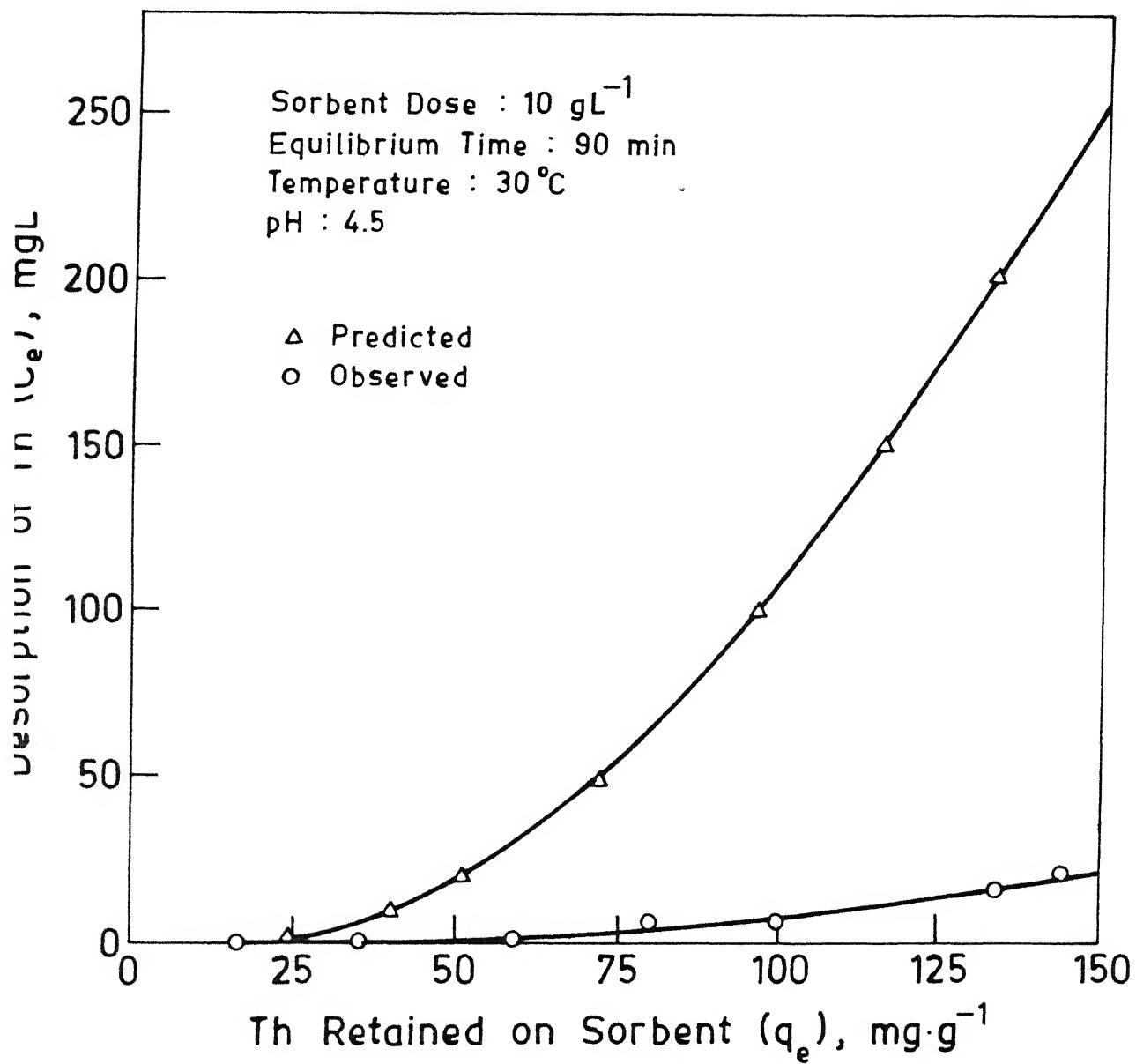


Fig. 5.8. Equilibrium Desorption of Th into Aqueous Phase from G. lucidum.

of actinide loaded G. lucidum as solid wastes. The desorbed biosorbent can be used for further processing the actinide bearing wastewaters. Hence, there is a need to study process of desorption of Th which represents the actinides, from G. lucidum by use of suitable eluants.

As Th complexes with the functional groups on G. lucidum, any ligand that forms a stronger complex with Th can be employed as an eluant. The presence of complexing anionic ligand like citrate, oxalate, pyrophosphate, mineral acids, Na_2CO_3 and NaHCO_3 have been found as suitable for desorbing uranium from the microbially based sorbents (Tsezos, 1984; Tsezos et al., 1989; Bhaskar et al., 1992). The potential of a mineral acid (H_2SO_4) and Na_2CO_3 to elute the sorbed Th from G. lucidum is evaluated and results are discussed.

5.5.2.1. Kinetics of Desorption of Th from G. lucidum Using 0.2 N Na_2CO_3

Figure 5.7 also presents the data on kinetics of desorption of Th from G. lucidum with an initial Th loading of 1.145 mg/g. Process of desorption is rapid with nearly 65% and 80% of initially loaded Th desorbing in 10 and 20 minutes respectively. The desorption was almost complete in 40 min, however, 90 min was adopted as equilibrium time.

5.5.2.2. Desorption of Th from G. lucidum Using H_2SO_4 and Na_2CO_3

As stated earlier H_2SO_4 and Na_2CO_3 have been employed to desorb Th from the biosorbent. The

process was carried out for 90 min and percent of Th desorbed by these eluants at different concentrations is presented in Figure 5.9. It is evident from the figure that Na_2CO_3 is better than H_2SO_4 at equimolar concentration. Even at a concentration of 1 N, the H_2SO_4 exhibited lesser desorption potential than 0.2 N Na_2CO_3 . The mode of action of H_2SO_4 appears to be the breaking of G. lucidum complex by the proton released from the acid; whereas CO_3^{2-} appears to form a much stronger complex with Th than that formed by G. lucidum during sorption process.

Bell *et al.* (1985), Bhaskar *et al.* (1992) have reported almost complete elution of sorbed U from R. arrhizus and G. lucidum with 0.5 N and 0.2 N Na_2CO_3 respectively. However for Th for a loading of 1.145 mg/g, the desorption is about 90%, less than that for uranium. Uranium is present mainly in hexavalent state and CO_3^{2-} form complexes with it. $\text{UO}_2(\text{CO}_3)_3^{4-}$ with $\log K_{\text{stab}}$ value of 22.3 being the final form in alkaline solutions (Ringbom, 1963; Katz *et al.*, 1986). The $\log K_{\text{stab}}$ for G. lucidum-U system is evaluated as 3.05 (Kulshrestha, 1992) which is much less than that for $\text{UO}_2(\text{CO}_3)_3^{4-}$. This is the reason for complete desorption of uranium from G. lucidum in the presence of CO_3^{2-} . However, thorium is present in tetravalent state which is reported to be the most stable of all tetravalent actinide. Although $\text{ThO}_2(\text{CO}_3)_3^{4-}$ complex is formed with CO_3^{2-} its $\log K_{\text{stab}}$ value is lower than that of U (Bagnall, 1972; Katz *et al.*, 1986). Lesser desorption of Th from G. lucidum with 0.2 N Na_2CO_3 than uranium is thus evident.

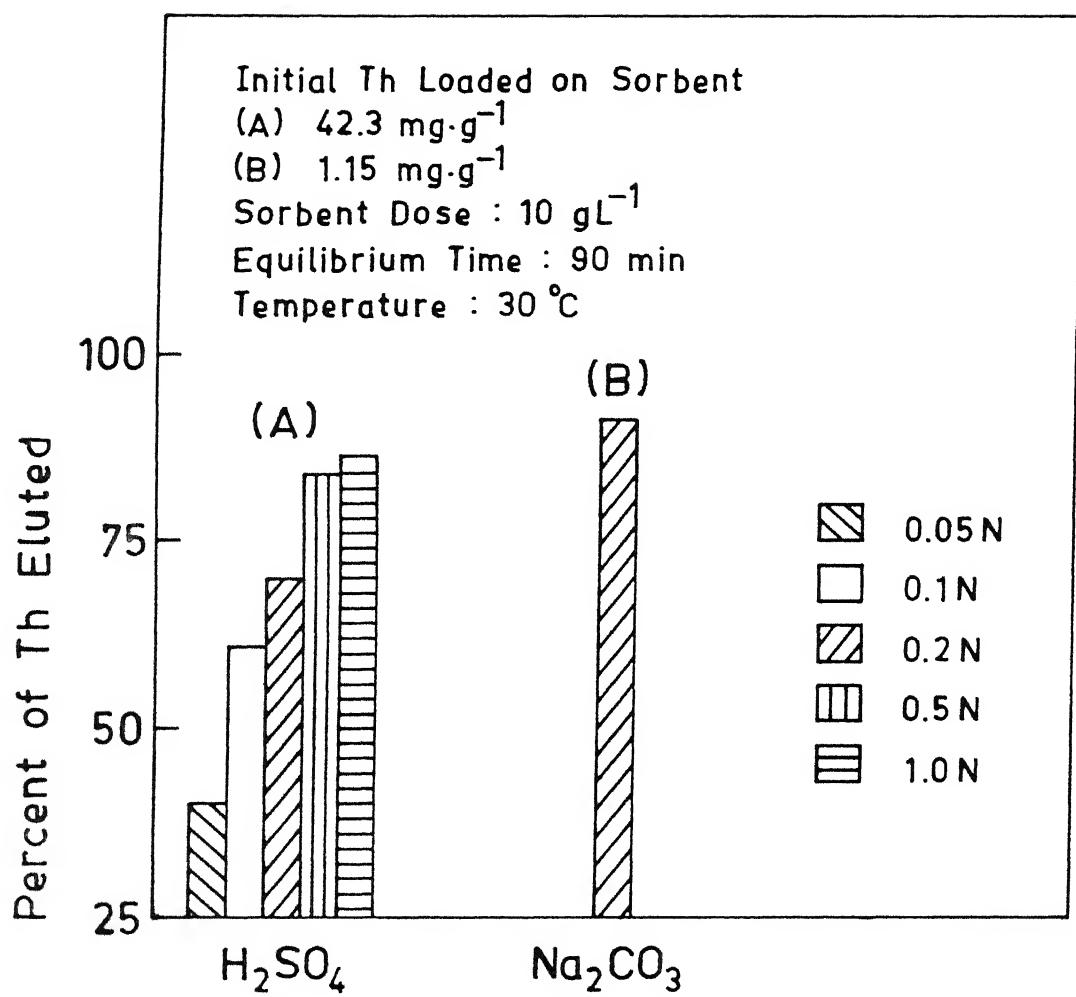


Fig. 5.9. Desorption of Th from *G. lucidum*.

5.6. Leachability of Th from Cement Concrete Blocks in Different Leachants

5.6.1. General

It has been shown in preceding section that fungal biomass G. lucidum is an efficient biosorbent for thorium at similar concentration as encountered in LLW (low level liquid waste). Its use in treatment of LLW will lead to generation of spent G. lucidum as wet solid radwaste. This has to be either desorbed or disposed off as solid waste in an environmentally friendly way.

It has been shown in the preceding section that desorption is possible with eluants (mineral acids, Na_2CO_3 etc.) leading to recovery of metal and facilitating the reuse of biosorbents. In mining of thorium and uranium the recovery of actinides (Th and U) by regeneration of ion-exchange resins is being practised (IAEA, Safety Series 44, 1976). Similar recovery of actinides from biosorbents may also be possible by desorption.

However, the recovery of actinides is generally not practised from the LLW from nuclear reactors because of the following reasons:

- (a) The LLW contains mainly fission products like Sr, Cs etc. along with the meagre amount of actinides (Eichholz, 1976). Thus desorbed solution is likely to contain a number of co-ions which would have to be selectively removed before Th could be recovered.
- (b) For meagre amount of thorium that can be removed from LLW the establishment of recovery system is likely to incur huge capital

(c) Liquid wastes from regeneration are often difficult to handle and this requires another stage to treat the regenerants liquids (IAEA, Technical Report, 1980). Thus regeneration of ion-exchange resins have proved uneconomical in nuclear power installations. Instead it is disposed off as solid waste (IAEA, Technical Report, 1980; Atabek, 1992).

Similarly it can be inferred that spent G. lucidum generated from the treatment of LLW would have to be disposed off as a solid waste. Immobilization technology is quite useful to isolate radionuclides from biosphere and solid waste management option often considers the cement matrix as a reliable barrier against the release of radionuclides (Zamorani, 1992). Therefore, cement was employed as a matrix for immobilization in the present investigation.

The resistance to leaching is the basic criteria to evaluate the quality of confinement (Atabek, 1992). These tests fall in two categories, namely, short-term and long-term leach tests. The long-term leach tests are used for safety assessment of the disposal proposals. The short-term leach test are primarily used for quality control, for the purposes of comparison of properties of various solidification products and to show the viability of proposal and hence to establish need for long-term tests.

As the extent of retention of radionuclides in cement matrix varies with each cement-waste formulation (Gilmore, 1977) and the knowledge of the effect of mixing cement with

G. lucidum is not known, the experiments to assess the viability of immobilization of spent G. lucidum in portland cement concrete without matrix modifiers (additives, plasticizers etc.) were undertaken in this study and the results are presented subsequently.

5.6.2. Cumulative Leachability in Various Leachants

The short term leaching tests were conducted using concrete blocks containing spent G. lucidum with 0.2 N Na_2CO_3 , 0.1 N HCl and simulated sea-water as leachant. The objective was to determine the effect of leachants on the leachability of Th confined in cement matrix and to assess the leaching mechanism. Further, these blocks are likely to be disposed in geological repositories where slightly acidic environment is encountered and oceans where alkaline environment exists, the use of Na_2CO_3 , HCl and simulated sea-water as leachants is justified.

Mishra *et al.* (1992) had earlier concluded from a similar study that the leaching of uranium was the least for cement concrete (CC) blocks in which loaded biomass was centrally placed rather than homogeneously distributed in concrete mix. For this reason, the biomass loaded with 43.3 mg of Th/g was placed centrally in each cube while casting. The cube thus cast, were subjected to 7 days of curing period during which the curing water samples were withdrawn and analysed daily to determine Th. The curing water did not have any detectable Th concentration even at the end of curing period signifying that no leaching has

occurred during curing period.

The cubes were, then, immersed in different leachants. Figure 5.10 illustrates the leachability of Th on a cumulative basis and the percent release of Th at the end of 9th day is presented in Table 5.5. It is evident from the figure that there was an initial rapid release reaching a plateau after 5 days. Considerable amount of Th leached in 0.2 N Na_2CO_3 and 0.1 N HCl whereas it was least in simulated sea-water. The high leachability from cement-concrete blocks in 0.2 N Na_2CO_3 and 0.1 N HCl may be attributed to chemical complexation of Th with CO_3^{2-} and protonation of G. lucidum with H^+ respectively.

Table 5.5

Cumulative Release (in percent) in Different Leachants at 9th Day

S.No.	Leachants	Cumulative percent leach $\text{C}/\text{C}_0 \times 100$
1	0.2 <u>N</u> Na_2CO_3	3.6%
2	0.1 <u>N</u> HCl	3.0%
3	Simulated sea-water	0.6%

Aalto and Ipatti (1992) carried out leach test on spent ion-exchange resins solidified in concrete (blast furnace cement) and observed the cumulative leaching for

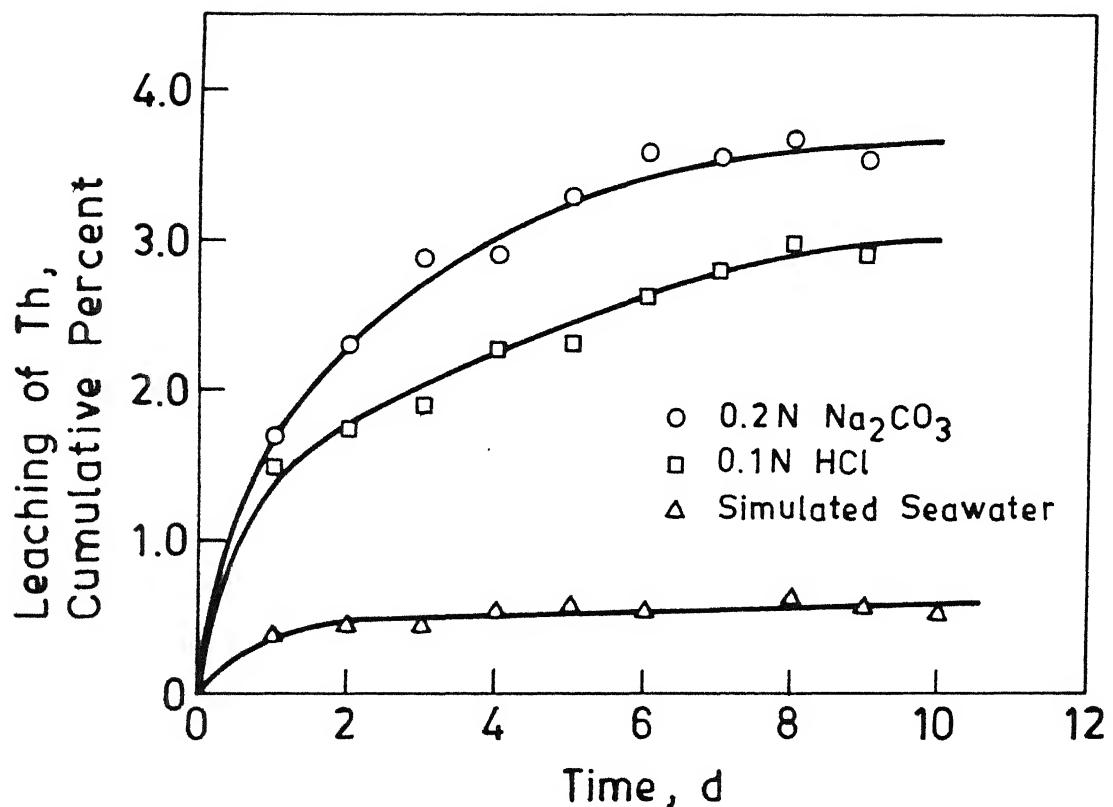


Fig. 5.10. Release of Th from CC Blocks in Different Solutions.

CS-137 and Sr-80 at the end of 9 days as 3.75% and 1% respectively with groundwater as leachant. Berner et al. (1992) theoretically predicted the leaching of uranium from cement-concrete blocks by simulated groundwater of Swiss repository as 10^{-7} M to 10^{-10} M and mentioned that it can be generalised to other actinides. The experimental value in present work for Th is 8.88×10^{-7} M at 9th day in simulated sea-water.

Thus cumulative leaching from cement-concrete blocks containing Th loaded G. lucidum is comparable to values cited in literature. Further, G. lucidum did not have any effect on compressive strength of cement-concrete blocks as verified by Mishra et al. (1992), thus, indicating good compatibility between them.

5.6.3. Empirical Relation for Leachability

As the life time of retention of actinide bearing wastes is around 300 years, a mathematical model based on the empirical data would facilitate to determine their long term behaviour. Hence, a plot of $\log C/C_0$ vs. $\log t$ is presented in Figure 5.11 yielding a straight line indicating that leaching is governed by the relation such as,

$$\frac{C}{C_0} = Bt^n \quad (5.6)$$

where C = Th released (mg) at t -th day

C_0 = Th loaded (mg) in G. lucidum

t = time in day

B = cumulative fraction Th released at 1st day.

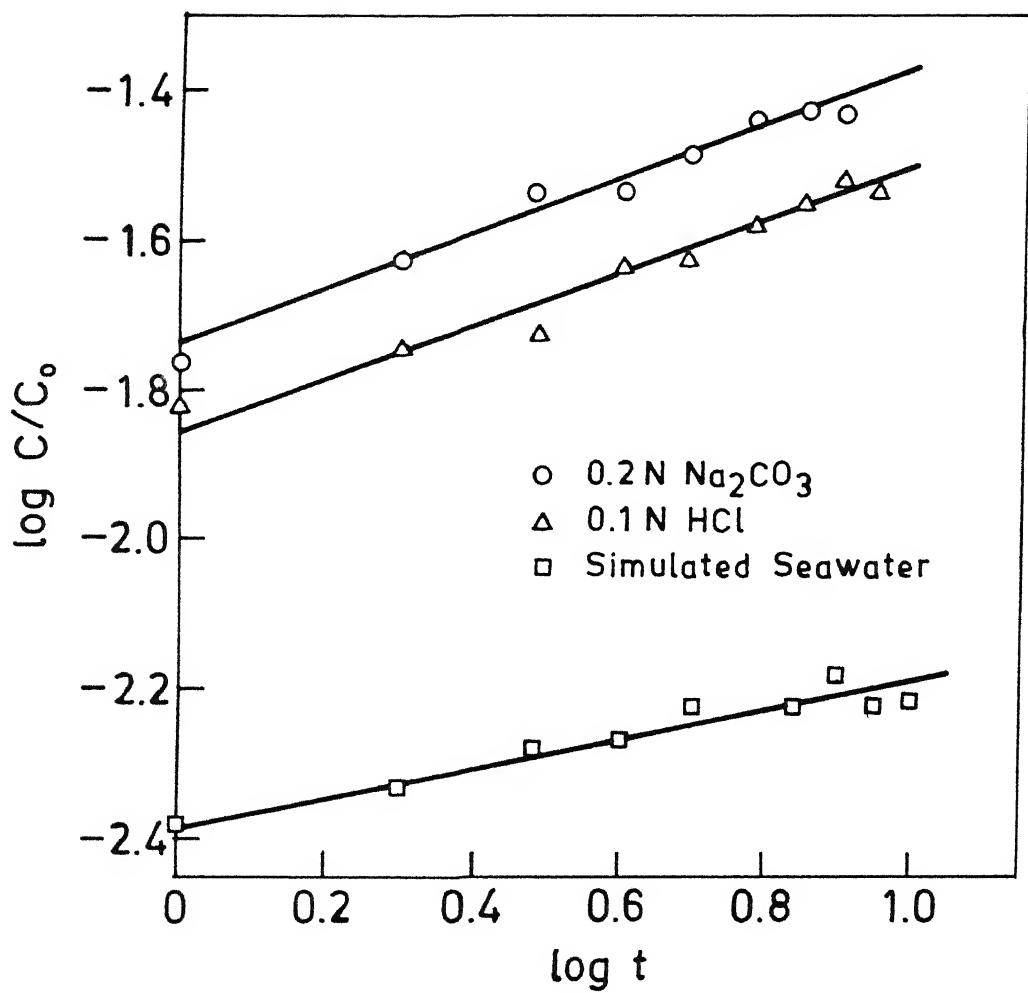


Fig. 5.11. Linearised Plot for Cumulative Fraction Release from CC Blocks.

Value of n are determined 0.4, 0.36 and 0.2 for 0.2 N Na_2CO_3 , 0.1 N HCl and simulated sea-water respectively. Equations and estimated percent release is given in Table 5.6. It has been suggested that if $n = 0.5$, then the leaching is governed by the diffusion (Zamorani, 1992). However, as this is not the case in the present study the release of Th may be due to combination of several mechanisms. It has been observed that the elements are carried through the matrix by advection, diffusion and possibly as mobile solid particles such as colloids (Atabek et al., 1992). During migration, Th may react with other dissolved components such as CO_3^{2-} to form a stronger complex. Th may also interact with solid surface of cement matrix via surface retention and ion-exchange, thus affecting the leaching.

Table 5.6

Empirical Relation and Estimated Leaching in Various Leachants

S.No.	Leachant	Equation	n	Percent $\text{^{th}}$ released			
				1 year	10 year	100 year	300 year
1.	0.2 M Na_2CO_3	$\frac{C}{C_0} = 0.018 t^{0.4}$	0.4	19	48	-	-
2.	0.1 M HCl	$\frac{C}{C_0} = 0.014 t^{0.36}$	0.36	12	27	61	91
3.	Simulated sea water	$\frac{C}{C_0} = 4.01 \times 10^{-3} t^{0.2}$	0.2	1.3	2.1	3.3	4.1

6. Summary and Conclusions

Investigation was conducted to determine potential of G. lucidum for treatment of LLW arising from various stages of nuclear fuel cycle. Thorium being potential nuclear fuel and representative of all other actinides (U, Np, Pu, etc.), was selected as model metal. Kinetic of sorption and equilibrium sorption studies in absence and in presence of co-ions at pH 4.5 have been conducted. Effect of HCO_3^- on Th uptake at pH 8 has been studied. Desorption employing sorption solution devoid of Th and other cluants was carried out. The short term leaching test were conducted on concrete cube containing spent G. lucidum incorporated in it.

Based on the results in the present investigation, the following conclusions may be drawn:

- (1) The kinetics of biosorption is very rapid with 90% of the sorption taking place in less than 10 min and attainment of equilibrium value in nearly one hour.
- (2) Equilibrium sorption studies reveal that the sorption process follow the Freundlich isotherm. The specific Th uptake is 130 mg/g for a residual Th concentration of 700 mg/L.
- (3) Co-ions Zn, Cu, Ni shows antagonistic effect on Th uptake though their effect was marginal.
- (4) Presence of HCO_3^- as high as 10 mM, decrease the Th uptake marginally at pH 8. Thus showing that G.

G. lucidum can remove actinides from alkaline liquor at its natural pH.

- (5) The process of desorption is also rapid with more than 90% recovery in less than 10 min.
- (6) Biosorption of Th by G. lucidum appears to be non-reversible process. The metal removal may be due to the chemical bonding between the metal and the ligand(s) on the surface of sorbents.
- (7) Na_2CO_3 and H_2SO_4 are found to be effective eluants desorbing almost 90% and 82% of the sorbed thorium respectively.
- (8) Cement concrete immobilization of spent G. lucidum and subsequent disposal in repositories or seabed is a viable proposal.

7. Suggestions for Future Work

The following suggestions may be made for future work:

- (1) Continuous flow studies on removal of Th.
- (2) Delineating the co-ordination environment of Th in the biosorbent.
- (3) Studies of biosorption of actinides from simulated sea water at pH 8.
- (4) Batch and continuous column studies on actual LLW containing Th from (i) mining and milling operations and (ii) nuclear reactors.
- (5) Optimisation of elution process using various concentrations and volumes of eluants for (i) Th solution, (ii) simulated LLW, and (iii) simulated sea water, containing actinides.
- (6) Long term leach test on spent G. lucidum immobilized in portland cement matrix, without additives.
- (7) Study to determine optimum cement-waste formulation.
- (8) Immobilization of spent G. lucidum in concrete matrix having additional constituents like: (a) supplementary cementitious materials e.g., natural pozzolanic materials, fly ash, silica, slag etc., and (b) matrix modifiers, i.e., plasticizers and additives like Ca(OH)_2 , Na_2SiO_3 , etc.
- (9) Organic polymer, i.e. polymer impregnated cement (P.I.C.).

- (10) Immobilization of spent biomass in different matrices like bitumen, U-F resins etc. and carrying out short term and long term leach tests.
- (11) Study of impact of redox conditions (E_h) on radionuclides release from solid matrix.
- (12) Modelling of cement degradation and radionuclides release.
- (13) Carrying out similar work for fission products like Cs, Sr, etc.

References

Aalto, H. and Ipatti, A. (1992). Leach Test of Spent Ion-Exchange Resins Solidified in Concrete. Cement and Concrete Research, 22, (2/3), 375-381.

Ashley, N.V. and Roach, D.J.W. (1990). Review of Biotechnology Applications to Nuclear Waste Treatment. J. Chem. Tech. Biotechnol., 49, 381-394.

Atabek, R., Bouniol, P., and Vitorge, P. (1992). Cement Use for Radioactive Waste Embedding and Disposal Purposes. Cement and Concrete Research, 22, (2/3), 419-431.

Bagnall, K.W. (1972). The Actinide Elements. Elsevier Publishing Company, New York, U.S.A.

Benjamin, G., Hezl, M.T., Hosea, J.M., and Darnall, D.W. (1986). Elimination of Bicarbonate Interference in Binding of U(VI) in Mill-Waters to Freeze Dried Chlorella Vulgaris. Biotechnol. & Bioengg., 28, 764-767.

Bermer, U.R. (1992). Thermodynamic Modelling of Cement Degradation: Impact of Redox Conditions on Radioactive Release. Cement and Concrete Research, 22, (2/3), 465-477.

Beveridge, T.J. (1978). Can. J. Microbiol., 24, 89. Cited in Muraleedharan, T.R. (1991). Current Science, 61, 6.

Beveridge, T.J. and Murray, R.G.E. (1980). Sites of Metal Adsorption in the Cell Wall of Bacillus subtilis. J. Bacteriol., 141, 876-887.

Beveridge, T.J. (1980). Metal Uptake by Bacterial Cell Walls. Paper presented at the Second Chemical Congress of ACS, Las Vegas, August 24-29. Cited in Tsezos, M. and Volesky, B., Biosorption of Uranium and Thorium, Biotechnol. & Bioengg., 23, 583-604.

Bhaskar, R. (1991). Biosorption of Uranium by Ganoderma lucidum. M.Tech. Thesis, Department of Chemical Engg., I.I.T., Kanpur.

Bhaskar, R., Agrawal, A.B.L., and Venkobachar, C. (1992). Biosorption of Uranium by Ganoderma lucidum. Presented at B.A.R.C., Bombay, February.

Brierly, J.A., Brierly, G.L., and Goyak, G.N. (1986). Fundamental and Applied Biohydrometallurgy. Eds. Lawrence, R.M., Branion, R.M.R., and Ebner, Amsterdam, 291.

Eichholz, G.G. (1976). Environmental Aspects of Nuclear Power. Ann Arbor Science Publishers, Inc., U.S.A.

Gilmore, W.R. (1977). Radioactive Waste Disposal. Pollution Technology Review No. 38, Noyes Data Corporation, New Jersey, U.S.A.

Guibal, E., Roulph, C., and Cloirec, P. (1992). Uranium Biosorption by a Filamentous Fungus *Mucor miehei*. Wat. Res., 26, 1139-1145.

Heacock, H.W. and Riches, J.W. (1974). Waste Solidification-Cement or Urea-Formaldehyde. Paper 74-WA/NE-9. Presented at ASME Winter Annual Meeting, New York. Cited in Gilmore, W.R., Radioactive Waste Disposal, Pollution Technology Review No. 38, Noyes Data Corporation, New Jersey, U.S.A.

IAEA (1963). Disposal of Radioactive Wastes into Fresh Water. Safety Series No. 10. International Atomic Energy Agency, Vienna.

IAEA (1966). Utilisation of Thorium in Power Reactors. Technical Reports Series No. 52. International Atomic Energy Agency, Vienna.

IAEA (1970). Thorium Fuel Cycle. Bibliographic Series No. 39. International Atomic Energy Agency, Vienna.

IAEA (1976). Management of Wastes from the Mining and Milling of Uranium and Thorium Ores. Safety Series No. 44. International Atomic Energy Agency, Vienna.

IAEA (1980). Guide to the Safe Handling of Radioactive Wastes at Nuclear Power Plants. Technical Reports Series No. 198. International Atomic Energy Agency, Vienna.

Ipatti, A. (1992). Solidification of Ion-Exchange Resins with Alkali-Activated Blast Furnace Slag. Cement and Concrete Research, 22, (2/3), Pergamon Press.

Katz, J.J., Seaborg, G.T., and Morss, L.R. (1986). The Chemistry of Actinides Elements, II, 1480-1547. Chapman and Hall, London.

Kulshrestha, M. (1992). Personal communication. M.Tech. student, Dept. of Civil Engg., I.I.T., Kanpur.

/b

Lamarsh, J.R. (1985). Introduction to Nuclear Reactor Engineering. Addison-Wesley Publishing Company Inc.

Manowitz, B. (1975). Development of Durable Long-Term Radioactive Waste Composite Materials. Progress Reports 7-10. Cited in Gilmore, W.R. (1977). Radioactive Waste Disposal, Noyes Data Corporation, U.S.A.

McKay, G. and Buro, M.J. (1988). Adsorption of Pollutants from Wastewater onto Activated Carbon Based on External Mass Transfer and Pore Diffusion. Wat. Res., 22, (3), 279-286.

Mishra, U.K., Goel, A.K., and Chauhan, M.S. (1992). Nuclear Waste Management by Biosorption. B.Tech. Project, Dept. of Civil Engg., I.I.T., Kanpur.

Muraleedharan, T.R., Iyengar, L., and Venkobachar, C. (1991) Biosorption: An Attractive Alternative for Metal Removal and Recovery. Current Science, 61, 6.

Muraleedharan, T.R. (1992). Personal communication. Ph.D. student, Dept. of Civil Engg., I.I.T., Kanpur.

Murray, R.L. (1988). Nuclear Energy. Pergamon Press.

Nakajima, A., Horikoshi, T., and Sakaguchi, T. (1977). Bippon Nogei Kagaku Kaishi, 51, 583. Cited from Chem. Abstr., 88, 59923.

Nakajima, A., Horikoshi, T., and Sakaguchi, T. (1978). Agr. Biol. Chem., 43, 625.

Norberg, A.B. and Persson, H. (1984). Accumulation of Heavy-Metal Ions by Zoogloea ramigera. Biotechnol. & Bioengg., 24, 239-246.

Norberg, A.B. and Rydin, S. (1984). Development of a Continuous Process for Metal Accumulation by Zoogloea ramigera. Biotechnol. & Bioengg., 24, 265-268.

Oyen, L.C. (1975). Solid Radwaste Systems. Presented at Georgia Institute of Technology. Cited by Gilmore, W.R. (1977). Radioactive Waste Disposal, Noyes Data Corporation, U.S.A.

Petrie, J.C., Donovan, R.I., Cook, R.E., and Christensen, W.R. (1976). Chem. Engg. Prog., 72, (4), 65.

Polikarpov, G.C. (1966). Radioecology of Aquatic Organisms. North-Holland, New York. Cited in Tsezos, M. and Volesky, B., Biosorption of Uranium and Thorium, Biotechnol. & Bioengg., 23, 583-604.

Rao, C.R.N., Iyengar, L., and Venkobachar, C. (1992). An Investigation of Cu(II) by Different Types of Waste Biomass, accepted for publication in JEED, ASCE.

Ringbom, A. (1963). Complexation in Analytical Chemistry. Interscience Publisher, New York, 293-338.

Ruchloft, C.C. (1949). The Possibilities of Disposal of Radioactive Wastes by Biological Treatment Methods. Sewage Works J., 21, 877-883.

Sharma, S.K. (1989). Biosorption of Copper(II) in a Fixed Bed Adsorber. M.Tech. Thesis, Dept. of Chemical Engg., I.I.T., Kanpur.

Shumate, S.E. and Strandberg, G.W. (1985). Comprehensive Biotechnology. Eds. Robinson, C.W. and Howell, J.A., Pergamon Press, 4, 235.

Strandberg, G.W., Shumate, S.E., and Parrot, J.R. (1981). Appl. Environ. Microbiol., 41, 237.

Tanaka, Y. (1970). Organic Macromolecular Binders of Metal Ions. Gastrointestinal Research Laboratory of McGill University, Montreal. Cited in Tsezos, M. and Volesky, B., Biosorption of Uranium and Thorium, Biotechnol. & Bioengg., 23, 583-604.

Tobin, J.M., Cooper, D.G., and Neufeld, R.J. (1987). Influence of Anions on Metal Adsorption by Rhizopus arrhizus. Biotechnol. & Bioengg., 30, 882-886.

Tsezos, M. and Volesky, B. (1981). Biosorption of Uranium and Thorium. Biotechnol. & Bioengg., 23, 583-604.

Tsezos, M. and Volesky, B. (1982a). The Mechanism of Uranium Biosorption by R. arrhizus. Biotechnol. & Bioengg., 24, 385-401.

Tsezos, M. and Volesky, B. (1982b). The Mechanism of Thorium Biosorption by R. arrhizus. Biotechnol. & Bioengg., 24, 385-401.

Tsezos, M. (1984). Recovery of Uranium from Biological Adsorbents-Desorption Equilibrium. Biotechnol. & Bioengg., 26, 973-981.

Tsezos, M., McCready, R.C.L., and Bell, J.P. (1989). The Continuous Recovery of Uranium from Biologically Leached Solutions Using Immobilized Biomass. Biotechnol. & Bioengg., 34, 10-17.

Tsezos, M. and Deutschmann, A.A. (1992). The Use of a

Mathematical Model for the Study of the Important Parameters in Immobilised Biomass Biosorption. J. Chem Tech. Biotech., 53, 1-12.

Volesky, B. (1987). Biosorbent for Metal Recovery. TIBTECH 5, 96-101.

Walton, D.G. (1989). Nuclear Engineer, 30, (6), 191.

Zamorani, E. (1992). Deeds and Misdeeds of Cement Composites in Waste Management. Cement and Concrete Research 22, (2/3), Pergamon Press.

Appendix A-1

Measurement of Complexation Parameters

The complexation reaction between a metal, M and a ligand, L, can be represented by $nM + L = \frac{M_n}{n}L$ where n is a positive integer. The equilibrium constant, K, for the reaction is given by

$$K = \frac{[M_n L]}{[M]^n [L]}$$

The complexation capacity and conditional stability constants of the sorbent can be evaluated by adding a range of metal concentrations to it in the absence of other possible competitive inorganic or organic ligands. Determination of conditional stability constants is usually dependent on measurement of the free and complexed (or sorbent bound) metal concentrations, M_f and M_b respectively, with no direct measurement of either the bound or free ligand concentrations (L_b and L_f , respectively). It is to be noted here that the sorbent is considered as a ligand with which the metal is complexed. If the complex has 1 : 1 stoichiometry then L_f can be expressed as $(L_t - M_b)$ and M_nL as M_b . Substitution of these values in equation and rearrangement yields the linear expression from which conditional stability constant, K' and complexation capacity can be calculated (Ruzic, 1982), i.e.,

$$\frac{M_f}{M_b} = \frac{M_f}{L_t} + \frac{1}{K' L_t}$$

A plot of M_b against M_f yields a rectangular hyperbola which is often described as "L-shaped". Thus, metal adsorption that correspond to an L-shaped isotherm could be representative of 1 : 1 complex formation. Further, by plotting the ratio of free to bound metal (M_f/M_b) versus free metal concentration (M_f), a straight line is obtained for which the slope is the inverse value of complexation capacity ($1/L_t$) and intercept is the inverse value of product of the conditional stability constant and the complexation capacity ($1/K'L_t$).

In the present investigation the biosorbent was equilibrated with a range of free metal ion concentration to yield a series of values for M_f and M_b , which were subsequently used for determination of complexation parameters.

Determination of complexation parameters (K' and L_t) was made by plotting the ratio $\frac{M_f}{M_b}$ versus M_f in Figure 5.12. G. lucidum appears to have the group(s) with $\log K'$ value of 3.02 L/mole. The complexation capacity L_t for G. lucidum is 376 mM/g.

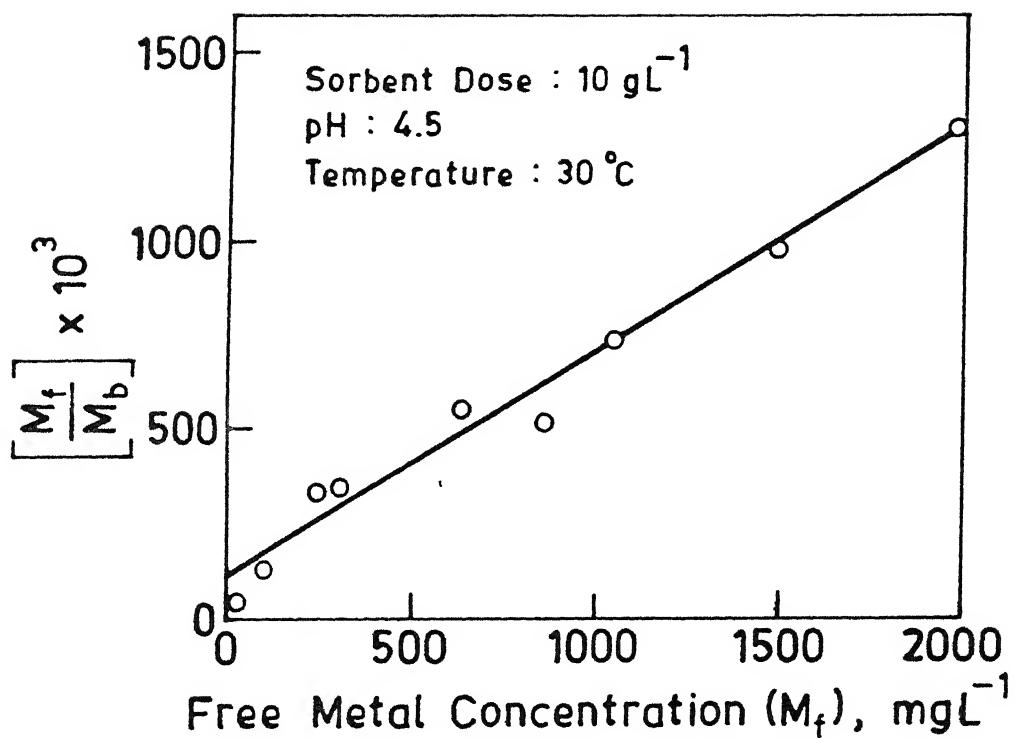


Fig. 5.12. Plot of Free Metal Concentration (M_f) vs. M_f/M_b .

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